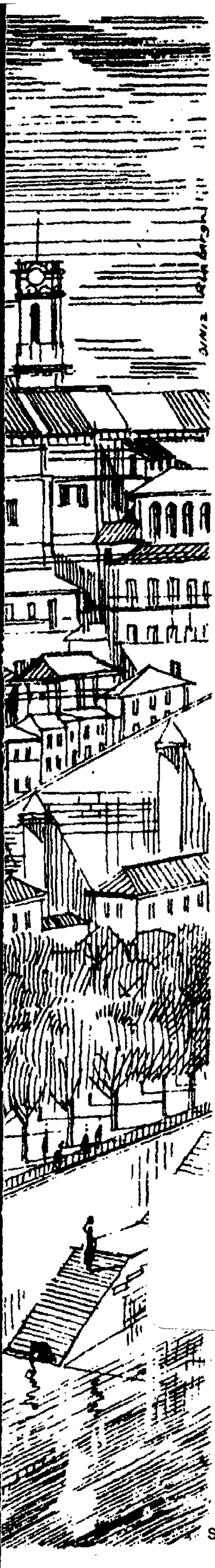

EUCMOS XXV

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XXV European Congress on Molecular Spectroscopy

BOOK OF ABSTRACTS

Edited by:

Rui Fausto
Elsa Diogo

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Coimbra - Portugal

Supported by the European Commission, Research DG - Human Potential Programme, High Level Scientific Conference 1999-

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XXV EUROPEAN CONGRESS ON MOLECULAR SPECTROSCOPY

COIMBRA - PORTUGAL
27 August - 1 September 2000

N68171-00-M-5878

SCIENTIFIC PROGRAMME

ABSTRACTS

LIST OF AUTHORS

Supported by the European Commission - Research DG - Human Potential Programme HPCF-CT-1999-00010

WELCOME

For the first time, the European Congress on Molecular Spectroscopy will be held in Portugal. It is very gratifying to know that leading scientists in the field of molecular spectroscopy will meet in Coimbra from 27th August to the 1st of September 2000 to present new research, make new contacts, exchange experiences and to define new objectives. Coimbra is a very beautiful and peaceful town situated on the Mondego River, approximately 185 km Northeast of Lisboa and 98 km Southeast of Porto. The city served as the capital of portugal from 1139 to 1385 and was the birthplace of six monarchs from the portuguese 1st Dynasty. Noted for its cultural tradictions and artistic treasures, Coimbra was long the intellectual capital of Portugal and remains one of its most important cities. The live of the city depends primarily on its University. As in medieval universities, the students wear long black capes and ribbons of varying colour to distinguish the various faculties. The institution was founded in 1290 and it is one of the oldest universities in Europe. Like an acropolis, the white buildings of the University of Coimbra now dominate the hilltop overlooking the north bank of Mondego. However, the University of Coimbra has been able to conciliate the past with both the present and future and it is also a "modern" university, very well equipped with up-to-date technology in the various fields of knowledge, and where science and technology are considered to play an essential role. The Science and Technology Faculty has actually more than 8000 students and more than 300 senior professors that dedicate to the most relevant brances of fundamental and applied science, being the largest and the most prominent faculty of the University. The Chemistry and the Physics Departments are certainly among the most important research centres in these fields of research in Portugal and both have since long ago attained the respect of the international scientific community.

I am sure that the outcome of EUCMOS XXV will be an important contribution to the progress of Chemistry and Physics, in particular of molecular spectroscopy, and that this meeting will confirm the excellence of the EUCMOS series, now cellebrating its 50th aniversair since the first event in Basel in 1951. It is a pleasure for me now, as chairman of EUCMOS XXV, to extend a warm invitation to you to attend the congress and wish you a very nice stay in Coimbra.

Rui Fausto, Ph.D.

Chairman of EUCMOS XXV

THE ORGANIZING COMMITTEES OF THIS CONFERENCE GRATEFULLY ACKNOWLEDGE SUPPORT FROM

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Thank very much the lecturers and
Participants by their valuable
Contribution to the scientific programme

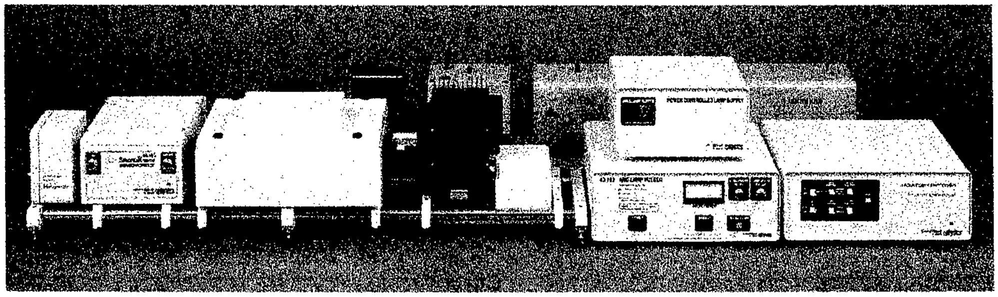
EUCMOS XXV
SCIENTIFIC PROGRAMME

TIMETABLE

	Sunday - 27	Monday - 28	Tuesday - 29	Wednesday -30	Thursday - 31	Friday - 1
9:00			PL5 R.N. Perutz	PL9 G. Smulevich	PL11 K.Hermansson	PL15 B. Lendl
9:30		Opening Cerimony				
10:00		PL1 - H. Kroto	PL6 - M. Rasanen	PL10 - P. Carey	PL12 - P.Pulay	PL16 -E.-H. Korte
11:00		Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:15		PL2 - P.J. Sarre	SL4 - R. Fausto	SL8- P. Hildebrant	SL10 - C.Castiglioni	SL14- M.L.Duarte
11:35			SL5 - B. v. d. Veken	SL9 - M.C. Costa	SL11 - C. Ogretir	PL17 - S. Turrell
12:00			OC A1 B1 C1 INT1	OC A4 B4 C4 INT4	OC A7 B7 C7 INT7	
12:20		SL1 E. Campbell	OC A2 B2 C2 INT2	OC A5 B5 C5 INT5	OC A8 B8 C8 INT8	
12:40			OC A3 B3 C3 INT3	OC A6 B6 c6 INT6	OC A9 B9 C9 INT9	Closing Cerimony
13:00		Lunch	Lunch	Lunch	Lunch	Lunch
14:30	Reception and Registration	PL3 G. Winnewisser	PL7 A.Moutinho	Excursion to Figueira da Foz	PL13 P. Hobza	
15:30		PL4 U.P. Wild	PL8 J. Finney		PL14 L.G. Arnaut	
16:30		Coffee Break	Coffee Break		Coffee Break	
16:45		SL2 J.P.Meier	SL6 - H. Burrows		SL12 - L. Ilharco	
17:05			SL7 - J. Mink		SL13 - M.G.Miguel	
17:25		SL3 F. Salama	Posters (I)		Posters (II)	
17:45						
18:00	Get Together Party	Reception: City Hall				
20:30					Dinner: St. Marcos	

ORAL CONTRIBUTIONS

	Low Temperature		***Solid State/New Materials***		***Astrophysics/Gas phase***		***INTAS***
A1	John Philis *(Greece)*	B1	James Durig *(USA)*	C1	Nick Westwood *(Canada)*	INTAS1	Natalia Strekal *(Belarus)*
A2	José Alonso *(Spain)*	B2	Czeslawa Paluszkiewicz *(Poland)*	C2	Maria Soukhoviya *(Ukraine)*	INTAS2	Sergey Maskevich *(Belarus)*
A3	Nadia Davidova *(Ukraine)*	B3	William Graham *(USA)*	C3	Karol Jackowski *(Poland)*	INTAS3	Alexei Feofanov *(Russia)*
	Biospectroscopy		***Biospectroscopy***		***Chemical Dynamics***		***INTAS***
A4	Alain Alix *(France)*	B4	Marcel Snels *(Italy)*	C4	Yves Marechal *(France)*	INTAS4	Vladimir Oleinikov *(Russia)*
A5	Vicenza Crupi *(Italy)*	B5	Simona Cinta-Pînzaru *(Romania)*	C5	Eli Pollak *(Israel)*	INTAS5	Alexander Kamnev *(Russia)*
A6	Hans Bettermann *(Germany)*	B6	Frauke Palmer *(Germany)*	C6	Valentina Venuti *(Italy)*	INTAS6	Mara Grube *(Latvia)*
	Theoretical Spectroscopy		***Computational Methods***		***Chemical Analysis***		***INTAS***
A7	Erik Svendsen *(Denmark)*	B7	Mozart Ramos *(Brasil)*	C7	Carmen Viets *(Germany)*	INTAS7	Vladimir Chirvony *(Belarus)*
A8	Nino Russo *(Italy)*	B8	Boris Galabov *(Bulgaria)*	C8	István Hannus *(Hungary)*	INTAS8	Vladimir Maleev *(Ukraine)*
A9	Natale Neto *(Italy)*	B9	Yurii Panchenko *(Russia)*	C9	Herbert Heise *(Germany)*	INTAS9	Sviatoslav Kirilov *(Ukraine)*



The LKS.60 spectrometer with Nd:YAG laser

EUCMOS XXV
LIST OF LECTURES AND POSTERS

MAIN PLENARY LECTURES

SHORT PLENARY LECTURES

ORAL CONTRIBUTIONS- A

ORAL CONTRIBUTIONS-B

ORAL CONTRIBUTIONS-C

ORAL CONTRIBUTIONS - INTAS

POSTERS SESSION (1) - TUESDAY 29th

1. SPECTROSCOPY IN ASTROPHYSICS

2. GAS PHASE/HIGH RESOLUTION SPECTROSCOPY AND MICROWAVE SPECTROSCOPY

3. LOW TEMPERATURE SPECTROSCOPY (MATRIX ISOLATION; LNG SPECTROSCOPY; SOLID STATE)

4. SPECTROSCOPY OF NEW MATERIALS

5. SOLID SATE SPECTROSCOPY (CRYSTALS; AMORPHOUS SOLIDS)

6. SPECTROSCOPY OF SURFACTANTS, MICELLES & LIQUID CRYSTALS

7. SPECTROSCOPY AND MOLECULAR STRUCTURE (SIMPLE ORGANIC MOLECULES; COMPLEXES)

8. SPECTROSCOPY & CHEMICAL DYNAMICS (1) (HYDROGEN BONDING; SOLVATION DYNAMICS; SOLVENT EFFECTS)

POSTERS SESSION (2) - THURSDAY 31st

9. SPECTROSCOPY AND CHEMICAL DYNAMICS (2) (CHEMICAL REACTIVITY; TRANSIENT SPECIES; PHOTOPHYSICHAL AND PHOTOCHEMICAL PROCESSES)

10. SPECTROSCOPY & CHEMICAL DYNAMICS (3) (MOLECULAR DYNAMICS; PHASE TRANSITIONS; DYNAMICS IN METAL ATOMS' CONTAINING SYSTEMS)

11. BIOSPECTROSCOPY (1) (PROTEINS & ENZYMES; NUCLEIC ACIDS; SUGARS & LIPIDS)

12. BIOSPECTROSCOPY (2) (BIO-SYSTEMS AND ORGANS)

13. BIOSPECTROSCOPY (3) (PHARMACEUTICALS)

14. THEORETICAL SPECTROSCOPY

15. COMPUTATIONAL METHODS IN SPECTROSCOPY (DIATOMICS & WEAKLY BOUND SYSTEMS; SIMPLE ORGANIC MOLECULES; H-BONDED SYSTEMS)

16. SPECTROSCOPY AND CHEMICAL ANALYSIS

17. LAST MINUTE CONFIRMATIONS...

ABSTRACTS
ORAL CONTRIBUTIONS - INTAS

SCIENCE PROGAMMES FOR TV AND THE INTERNET IN THE 21st CENTURY

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Even though Science is the dominant culture of the 20th Century and looks destined to become even more dominant in the 21st, this dominance as well as the cultural nature of science are poorly appreciated by the Public as well as many in the Business World and Government. Major problems arise in the way the Media propogate Science with semi-realistic paranormal programmes and bizarrely stereotyped images of Scientists. Some efforts to adress the problems are being initiated via the Vega Science Trust (www.vega.org.uk) which aims to take advantage of the revolution in TV and digital communications and create a platform for the science, engineering and technology (SET) community to communicate on their advances, excitements and concerns. The best scientists and science communicators are being recorded and the programmes being broadcast on BBC-TV. Furthermore School/University outreach programmes are being developed. Webcasting in particular offers the promise of democratising broadcasting and allows the SET community to focus on its own perspective – which is of couse the one which led to the technolgical foundation of everyday life. These efforts present a perspective on Science which places the cultural factors in the foreground and focuses on the intrinsic charisma of science which is hidden from many. It is now crucial that the society in general and the scientific community in particular accept that a real intellectual problem is involved. In this lecture segments from our programmes and those of others are presented to show how the new technologies may help to solve the problems. Science is part of our cultural heritage and even a modest understanding sometimes requires some detailed knowledge of the "language" of science as a vehicle for the communication of ideas.

PL2

THE DIFFUSE INTERSTELLAR BANDS

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The unidentified diffuse interstellar absorption bands are observed in near-UV, visible and near-IR spectra recorded towards stars that are partially obscured by interstellar dust. Their origin is the longest standing problem in astronomical spectroscopy and dates back to the 1930s when systematic study of the bands first started. The absorptions are known as diffuse bands because their widths are greater than those arising from transitions in known atoms and molecules observed along the same lines of sight.

There has been a lively controversy as to whether the carriers are free gas phase molecules or are associated with the dust which causes the extinction of starlight. Proposals for the carriers range from molecular hydrogen to porphyrins and from colour centres to species adsorbed on grains. Evidence considered to be in favour of molecules as carriers has grown in recent years and includes the invariance of the wavelengths and narrowness of some of the bands, the lack of polarization structure, and the discovery that some of the bands are seen in emission from a peculiar nebula, the `Red Rectangle', and an R CrB star V854 Cen at minimum light.

Recent observations include wavelength and spatially resolved `diffuse band' emission from the Red Rectangle, complementary studies of the 3.3 micron `unidentified' infrared (UIR) emission band, and ultra-high resolution absorption spectra of some of the bands which are found to exhibit fine structure. A hypothesis that some of the bands may arise from rovibronic transitions between the ground states of negatively charged molecules and/or small grains and shallow dipole-bound electronic states which lie close to the electron detachment threshold will be described.

SPECTROSCOPY OF THE HEAVENS
FROM PRESENT STAR FORMATION TO THE EARLY UNIVERSE

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Spectroscopy of the heavens started in 1814, the year Joseph von Fraunhofer had discovered in the optical region of the solar spectrum a large number of absorption lines. Partially identified by Kirchoff and Bunsen in 1860, it turned out that the carriers of these Fraunhofer lines were caused by atoms in the chromosphere of the Sun. Fraunhofer's discovery marks probably the earliest and one of the greatest achievements in spectroscopy. As Kirchhoff and Bunsen noted in one of their papers that the "almost inconceivable" sensitivity of spectroscopy would open "an entirely untrodden field, stretching far beyond the Earth or even the solar system".

With the recent opening of highly sensitive laboratory and interstellar spectroscopy in the terahertz region (frequency $\nu = 1$ THz corresponds to wavelength $\lambda = 0.3$ mm), great scientific advances can be expected, amongst which are (i) a new look at the rotational spectra of light hydrides and other molecules, radicals, and ions, (ii) low energy bending vibrations of larger (linear) molecules and ring-puckering motions of notably polycyclic aromatic hydrocarbons, (iii) the class of very weakly-bound van der Waals complexes, and many more.

At present, more than 120 molecular species have been identified in interstellar clouds and circumstellar envelopes, presenting evidence of a rich and very diversified chemistry. Carbon monoxide, CO, together with its various isotopomers (including double substitutions) is the most abundant and ubiquitous molecule in space with rotational transitions throughout the millimeter- and submillimeter-wave region. Together with other diatomic and simple polyatomic molecules, radicals, and positive ions, CO is found throughout molecular clouds in the Universe, whereas the more complex molecules are restricted to high density cores of molecular clouds and to low -temperature cocoons of protostars in the Milky Way. These studies will finally allow, together with the new instrumentation planed (ALMA = **A**tacama **L**arge **M**illimeter **A**rray), to follow observationally how gas and dust evolves from a collapsing cloud core into a circumstellar disk. Out of the disk form stars and planets. In the wake of the birth of newly-formed stars positioned near the center of disks, planets can form in and from the remaining disk material .

The more than 1000 spectral lines in the millimeter- and submillimeter-wave region have become a unique tool to trace molecules far away in young, high redshift galaxies in the early universe. The discovery of CO in the galaxy IRAS F10214+4724 has opened the distant universe to observational scrutiny by molecular transitions. Since then, CO has been detected in the gravitationally lensed Cloverleaf quasar at redshift $z = 2.56$. It is however most remarkable that large amounts of CO and dust are present already at $z = 4.7$. This value for the redshift corresponds to a look-back time of 92% of the age of the universe and shows that enrichment of the interstellar medium occurred already at very early epochs. These lines allow to estimate the mass, density, velocity spread, and kinetic temperature of the cold moleclar gas at these early epochs of galaxy evolution.

PL4

SINGLE MOLECULE SPECTROSCOPY, MICROSCOPY AND IDENTIFICATION

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Single Molecule High Resolution Spectroscopy at very low temperature provides information about structure and dynamics in solids unveiling fascinating effects which could not have been observed on bulk samples. The behavior of each molecule is unique since it depends strongly on its local environment. Many individual single molecules have to be investigated to obtain the distribution of parameters of single molecule properties.

First, a short introduction into the methods of Single Molecule Detection and Spectroscopy will be given. Electric field and pressure effects will be discussed. New results obtained at 30 mK which relate to the freezing in of the dephasing processes are presented. Most of the experiments are performed by Fluorescence Excitation Spectroscopy. Recent measurements allow, however, also a direct observation of the absorption profile of a single molecule with good signal-to-noise.

Fluorescence microscopy of the classical wide field type, as well using scanning probe microscopes, are employed in specific single molecule applications.

Very recently experimental studies concerning single molecule identification by time and spectrally resolved excitation spectroscopy are presented. The main point is the challenge to record and to analyze the whole information that every single emitted photon carries. Meeting this challenge opens the possibility to identify specifically chosen single molecules at room temperature with just a few photons.

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PHOTOCHEMISTRY OF METAL HYDRIDE COMPLEXES

PL5

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Many transition metal complexes containing carbonyl and ethene ligands are photosensitive. The resulting photofragments are astonishingly reactive: some coordinate weak donors such as xenon, alkanes and silanes [1]. Others undergo oxidative addition at the H–H bond of hydrogen or C–H bonds of alkanes and arenes. Metal dihydride complexes with the hydride ligands *cis* to one another have also proved particularly effective for such photochemical reactions [2]. Examples include $W(\eta^5\text{-}C_5H_5)_2H_2$, $Ru(dmpe)_2H_2$, $Rh(\eta^5\text{-}C_5Me_5)(PMe_3)H_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) Such complexes and their ultimate photoproducts are ideal for studying by NMR spectroscopy. Laser flash photolysis with UV/vis detection can provide a wealth of kinetic information on short-lived reaction intermediates.

A good example is provided by $Ru(PP_3)(H)_2$ where PP_3 is a chelating tetradentate phosphine $[P(CH_2CH_2PPh_2)_3]$ which remains fully bound during the reactions, constrains the geometry of the reaction intermediates, and modulates their reactivity through the presence of the phenyl substituents [3]. The resulting reactive intermediate, $Ru(PP_3)$, undergoes intermolecular reaction with benzene in an alkane solvent within microseconds in preference to intramolecular reaction. The reactivity of the osmium analogue is even more unusual: it undergoes selective reaction with alkanes with terminal methyl groups to form alkyl hydride complexes [3].

If a carbonyl group is incorporated in the precursor, or the photofragment is allowed to react with CO, time-resolved infrared (TRIR) spectroscopy may be employed. The CO stretching band acts as a marker of structure and oxidation state. Precursor complexes with two hydride ligands and a carbonyl ligand typically undergo photochemical loss of H_2 in preference to CO loss. It was by studying an example of this type, $Ru(PPh_3)_3(CO)(H)_2$, that we were able to demonstrate through ultrafast vibrational spectroscopy that loss of H_2 is complete within 10 ps [4].

Two photochemical pathways are active in the case of $Ru(PMe_3)_4(H)_2$, loss of H_2 and loss of PMe_3. Earlier studies concentrated on the product with trialkylsilanes and created the illusion that loss of PMe_3 was the only pathway. When we investigated the reactivity by time-resolved spectroscopy, the H_2 loss-pathway was revealed. Product studies with dialkylsilanes confirmed this conclusion.

Time-resolved spectroscopy has provided strong evidence for precoordination of arenes to transition metal species before the C–H insertion step. If benzene is replaced by naphthalene, the η^2-arene complex is stabilised. Its molecular conformation in solution can be deduced by NOESY spectroscopy, while the dynamics of its fluxional behaviour are revealed by the related EXSY method [5]. Quantitative analysis of the NOESY spectra allows the mean distance between some of the hydrogen atoms to be determined in solution. Such distances are close to crystallographically determined values.

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PL6

NEW RARE GAS CHEMISTRY

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In recent few years we have characterized both by infrared matrix isolation spectroscopy and extensive ab initio calculations a new class of rare gas containing molecules of general formula HrgY,[1-3].

The molecules studied are HXeI, HXeBr, HXeCl, HXeH, HXeCN, HXeNCO, HXeSH and HXeOH as well as HKrCl and HKrCN. These molecules form after UV-photolysis of a suitable hydride HY and thermal mobilization of the H-atoms. The formation from neutral fragments was shown by infrared photodissociation experiments where selective pumping of the v = 3 of the H-Xe streching mode of HXeI resulted in decomposition of the Molecule [4].

Concerning geometries of these hydrides we have to rely on ab initio calculations. Bond formation for example in HXeI decreases the H-Xe and Xe-I distances by more than a factor of 2 and 1.5, respectively from the van der Waals distances of the constituent atoms. The bonding consists both of covalent and ionic contributions, and in the Xe compounds the central rare gas atom has typically +0.6 - +0.7 local charge. The large dipole moment explains the extremely strong infrared H-Rg absorptions, being several thousands of km/mol.

The synthesis, spectroscopic characterization, ab initio calculations,and origin of bonding of the hydrides will be discussed. In addition, the cosequences of the potential minimum due to the metastable HRgY molecule upon photodissociation and light induced and thermal mobility of the hydrogen atoms in solid xenon will be discussed.

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PROBING MOLECULAR BEHAVIOR BY LOW ENERGY PARTICLE SCATTERING

PL7

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Low energy particle scattering is a means of obtaining information about the molecular behavior in any media, gaseous, liquid or solid. The collision event probes the system in a very short time and in its real scale. The processes occurring during the collision can be identified by measurements of the resulting species and their charge state. Measuring the energy and angular distributions of the scattered particles one may get structural information. In this context surface techniques such as low energy ion scattering (LEIS), secondary ion mass spectrometry (SIMS) and particle (electron or ion) stimulated desorption are often used. To illustrate several of the features of such collision experiments some examples will be presented.

Recently an increasing number of studies have been performed on non-metallic surfaces including liquid surfaces. One example will focus on the interaction of a projectile (rare gas ions and electrons) with a liquid polymeric surface of perfluorpolyether (PFPE). This polymer has the approximated formula $F[CF(CF_3)CF_2O]_{63}CF_2CF_3$, is liquid at room temperature and has extremely low vapor pressure. Therefore it can be probed by surface analysis techniques in ultra high vacuum. Measurements of the yields of the ionized emitted species, their energy and angular distributions evidenced the structure of the macromolecule and the way how the projectile energy is dissipated in the media and how the PFPE fragments.

ENZYME ACTIVITY AND MOLECULAR MOBILITY: TIME SCALES AND SOLVENT EFFECTS

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It is widely accepted that enzymes require internal flexibility for catalytic activity. Measurements using a number of spectroscopic and scattering methods have revealed a temperature-dependent transition in equilibrium dynamical fluctuations of several proteins at around 200-220K[1,2]. Below this transition, the enzyme motions are thought to be mostly vibrational, while above it, anharmonic dynamics are observed. Although correlations have been observed between protein functions such as ligand binding or proton pumping and the presence of anharmonic motions, the time scales and forms of the functionally important motions for enzyme activity remain poorly understood.

In a series of parallel measurements of enzyme motions and enzyme activity, we have examined the time scale and solvent dependence of the dynamical transition, and the relation between changes in the dynamical behaviour of the enzyme and the onset of activity. Dynamic neutron scattering results on a glutamate dehydrogenase (GDH) show that *enzyme activity remains at temperatures below the dynamical transition*[3]: although a transition is observed at ~220K, the enzyme activity shows no significant deviation from Arrhenius behaviour down to 190K. Thus, the observed transition in the enzyme's dynamics is decoupled from the rate-limiting step along the reaction coordinate. Further work using neutron spectrometers of different energy resolution showed a marked time scale dependence of the dynamical transition, with several such transitions observed on the nanosecond time scale[4]. Comparison with the temperature profile of the enzyme activity again showed the presence of several dynamical transitions that had no effect on GDH function.

Very recent measurements of the dynamics of a thermophilic xylanase enzyme in a range of solvents showed that the general features of the dynamical transition of protein solutions follow those of the solvent. However, the differences between the dynamical behaviours of the various cryosolvent protein solutions themselves are remarkably small. These results suggest that the short timescale protein dynamics may be relatively insensitive to significant changes in the solvent composition. Some possible implications of these results for solvent effects on enzyme dynamics and activity are discussed.

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SPECTROSCOPIC VERSUS CRYSTALLOGRAPHIC INFORMATION ON THE STRUCTURE OF THE ACTIVE SITE OF PEROXIDASES

PL9

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Plant peroxidases are heme-containing enzymes involved in a wide range of biological functions. They are divided into three classes on the basis of sequence alignment (1). They constitute one of the most studied groups of enzymes, not only for their biomedical and industrial applications, but also because of their inherent spectroscopic properties. Moreover, the recently solved crystal structures and the contribution of site-directed mutagenesis have shed new light on the structure-function relationship of these enzymes.

The present work reviews the electronic absorption and RR studies of plant peroxidases with particular attention being given to recently established novel spectroscopic markers (2). Spectroscopic differences are observed between the three classes. In particular, class III is characterized by the presence at room and low temperatures of a quantum mechanically mixed-spin state due to admixture of high-spin (S=5/2) and intermediate-spin (S= 3/2) heme states (3).

Comparison of the spectroscopic data with the available X-ray structures provides a detailed insight into the role played by the heme cavity residues in peroxidase function and stability. However, the spectroscopic results and X-ray crystal structures will be critically analyzed and the differences existing between the crystal and the solution states underlined.

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PL10

RAMAN SPECTROSCOPY'S ROLE IN MOLECULAR MEDICINE

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Recent advances in technology have brought about a near-revolution in the application of Raman spectroscopy to biological problems. The twin problems of low sensitivity and fluorescence interference have essentially disappeared with the use of high throughput spectrometers and deep-red excitation sources (1,2). Thus, Raman spectroscopy stands poised to take its place alongside techniques such as X-ray crystallography and NMR in structural biology. The present lecture will deal with two areas that are of importance in molecular medicine – the understanding and control of disease states at the molecular level.

The first topic addresses the utility of Raman spectroscopy in drug design. The enzyme urokinase is a major target in the pharmaceutical industry for the design of inhibitors since urokinase is a central player in cancer progression. Raman data will be presented for a number of drug-candidate complexes with urokinase in the 100 micromolar concentration range. The data will be interpreted in concert with the X-ray derived structures determined by our industrial collaborators. A general problem in biophysics in general and in drug design, in particular, is relating structures derived in single protein crystals to those found in vivo – i.e. in solution. Raman data have great potential for bridging this gap and we will show how chemical reactions and conformational changes can be followed in minute single protein crystals.

The second topic involves the elucidation of the molecular mechanism of a disease process itself. Several proteins have the ability to undergo large conformational changes and to convert from their biologically functional soluble form to insoluble pathenogenic plaques. The best known of these are prion proteins that have been identified in Alzeimer's disease and the neural plaques that are found in the brains of animals that have suffered "mad cow" disease. Although resistant to most methods in structural biology, the plaques, or insoluble fibrils, can provide high quality Raman data. In turn, these provide novel and valuable insight into the structure of the fibrils making up the plaques and into their mechanism of formation.

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VIBRATIONAL SPECTROSCOPY IN THE CONDENSED PHASES - FROM THEORETICAL CALCULATIONS

PL11

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Intramolecular frequency shifts are powerful probes of a molecule's chemical environment. In liquids and solids, the shifts observed are usually the result of interactions with many neighbours, close by and further away, stationary in space or moving. Theoretical calculations - quantum-chemical calculations at 0 K and dynamical simulations at elevated temperatures - can help us interpret the origin of the experimental shifts.

In addition to intramolecular frequency shifts, I will discuss other types of molecular motion, such as the diffusive and rotational motion of solvent molecules around ions in solution, and the librational motion of water molecules in the crystalline state.

PL12

ACCURATE SCALED QUANTUM MECHANICAL (SQM) FORCE CONSTANTS AND VIBRATIONAL SPECTRA OF TRANSITION METAL COMPLEXES WITH HARD LIGANDS

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Transition metal complexes are important in many areas but their theoretical treatment had been plagued by several difficulties: (1) strong electron correlation effects, particularly for first-row transition metals; (2) the considerable size of these molecules makes the calculations too expensive, and (3) the complexes are often charged, making benchmarking using isolated molecules inaccurate, or, for multiply negatively charged ions, impossible.

Recent advances have contributed much toward the solution of these problems. In spite of its slightly semiempirical character, density functional theory, using gradient-corrected exchange-correlation functionals, provides an efficient and accurate method for treating transition metals. Parallel arrays of personal computers easily achieve supercomputer performance at a fraction of their cost. Finally, most benchmark calculations have been performed on uncharged π complexes which are often electrically neutral. However, the latter are not representative of transition metals in biological systems which are often coordinated by hard ligands - oxygen and nitrogen.

This talk summarizes our results in developing Scaled Quantum Mechanical [1] (SQM) force fields for, and predicting the vibrational spectra of, first-row transition metal porphyrin [1], phthalocyanine and acetonylacetonate (acac) complexes. All recent calculations have been performed on an array of networked high-end personal computers, using the PQS [1] software. The molecules selected have hard ligands but are neutral overall, facilitating comparison with experiment. Scale factors have been developed for coordinates involving the metal-ligand bond to augment standard organic scale factors[1]. Predicted band positions are in excellent agreement with experiment, while predicted intensities are qualitatively correct.

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IMPROPER, BLUE-SHIFTING HYDROGEN BOND

PL13

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Accurate ab initio calculations revealed a new type of intermolecular binding which resembles the standard hydrogen bonding. Because, however, the manifestation of this new type of binding is opposite to the standard hydrogen bonding and also its nature differs from the nature of standard hydrogen bonding, this new type of binding is called improper, blue-shifting hydrogen bonding. Standard hydrogen bonding of the type X-H...Y is typical with weakening of the X-H bond which is consequently followed by elongationof this bond and a red shift of the X-H stretch frequency. Improper, blue-shifting X-H...Y hydrogen bond is, on the other hand, characteristic by strengthening of the X-H bond, which yields contraction of this bond and a blue shift of the X-H strech frequency.

PL14

THE INTERSECTING-STATE MODEL: A LINK BETWEEN MOLECULAR SPECTROSCOPY AND CHEMICAL REACTIVITY

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The view that the ability of molecules to react rests ultimately on their own structural properties has long been dear to chemists. Although the encounter of two molecules triggers unique features which neither molecule possesses alone, the notion that molecules contain all the information necessary to understand their reactivity has proved extremely useful. Chemical reactivity can be understood both as the ability of individual molecules to take part in various chemical reactions as well as the rates of such reactions, that is, equilibrium and rate processes. This contribution is focused on rate constants and on the fact that their value for the understanding of chemical reactivity reflects our ability to relate them with reaction energies and molecular structure.

Chemical reactivity depends on energy relationships along the reaction co-ordinate. Although central to chemical reactivity, the "reaction co-ordinate" of a given reaction, in the absence of a potential energy surface (PES), largely remains an educated guess. Ideally we would like to have analytical expressions for the variation of the potential energy along the reaction path. Then, transition-state structures could be characterised and reaction mechanisms elucidated.

The Intersecting-State Model (ISM) formulates a general relationship between reactant and transition-state structures, scaled with the transition-state structure of an accurate $H+H_2$ PES. ISM can be used to calculate the barrier heights of atom-transfer reactions in the gas phase, $A+BC \rightarrow AB+C$, using spectroscopic information on the B–H and A–H Morse curves and a reaction co-ordinate given by the valency of those bonds. ISM provides a link between the molecular structure of the reactants and their reactivity and offers a clear insight of the role of molecular parameters such as bond lengths, force constants, bond orders or bond dissociation energies in the making of reaction energy barriers. The understanding of such factors paves the way to define families of reactions and calculate their intrinsic energy barriers.

We offer a guided tour in the fascinating world of chemical reactivity, starting from the simplest system ($H+H_2$ in the gas phase) to arrive at complex biological systems pivotal to the making of live (electron transfer in photosynthetic reaction centres). The view emerging from our tour is that chemical reactivity results from an interplay of structural factors (bond lengths), spectroscopic behaviour (force constants), electronic indices (bond orders) and thermodynamic factors (reaction energies). ISM integrates all these factors in a physically sound model, with a microscopic relation to the topology of PES and very simple to use.

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FLOW INJECTION ANALYSIS COUPLED TO VIBRATIONAL SPECTROSCOPY: A POWERFUL TOOL FOR PROBLEM SOLVING IN ANALYTICAL CHEMISTRY

PL15

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This contribution aims to highlight benefits gained from the combination of vibrational spectroscopic detectors with flow injection analysis (FIA) by reporting recent results in the fields of process analysis, time resolved infrared spectroscopy and surface enhanced Raman spectroscopy.

In the first example a fully automated FIA-ATR-FTIR system for fermentation control is presented. The process investigated was the Acetone-Butanol-Ethanol (ABE) fermentation which has attracted renewed interest recently as an alternative and environmentally friendly method for the production of solvents. Using an automated flow injection system problems arising from biofouling of the sensing surface (ATR), pH variation during the fermentation as well as gas formation could be solved making the continuous monitoring of 6 target analytes during complete feed batch fermentations possible.

In the second example an universal approach for fast time resolved MIR spectroscopy of arbitrary chemical reactions in solution based on a specially developed multi-sheath flow mixer is presented. The micro-machined mixer is made of polymers and produced on top of IR transparent CaF_2 windows. The developed mixer produces out of two macroscopic streamlines an alternating sequence of micro-streamlines (width below 20 µm). Due to the short residence time (below 1 ms) of the stream lines in the flow cell and due to the fact that strongly laminar conditions prevail hardly any mixing occurs as long as the flow is maintained. However, upon stopping the flow rapid diffusion based mixing occurs which allows to initiate any chemical reaction of interest and to follow the reaction dynamics on a molecular basis. In this presentation the principles of the new technique will be outlined as well as first data on selected chemical reactions shown.

The third examples reports on a new approach for reproducible SERS measurement in solution using SERS active micro-beads which were produced on-line by chemical reduction of $AgNO_3$ and deposition of the produced silver particles on Sephadex micro-beads using an automated flow system. These SERS active beads were brought in contact with the analyte (nicotinic acid) and retained for measurement in a specially designed flow-cell. Afterwards the SERS-micro-beads were discarded by flow reversal and new, freshly prepared SERS-micro-beads together with the analyte could be introduced automatically into the flow system. In this way regeneration of the SERS active surface could be avoided as fresh, unused beads were available for every measurement. The developed method is characterized by complete computer control of all operation steps, high sensitivity of the SERS measurement, high precision and long-term stability.

PL16

CHARACTERIZATION OF NANOMETER LAYERS BY INFRARED SPECTROSCOPIC ELLIPSOMETRY

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Thin layers on the surface of bulk material find wide application in science and technology. The field stretches from micrometer-thick coatings for visual or hygienic purposes, and implantations to improve mechanical or electronic properties, down to fractions of a monolayer of atoms or molecules such as passivation layers or specifically activated surface sites. On one hand, the demand for sensitivity of the experimental method increases with decreasing coverage. On the other hand, a layer can only be realized as a layer if its backside, i.e. the interface between layer and substrate, contributes to the evaluated signal. Therefore, from a spectroscopic point of view it is favourable if layers are the thinner the stronger absorbing they are.

Ellipsometry is well established as a non-destructive technique to characterize thin layers. In industrial routine mostly one wavelength in the visible range is employed to determine the polarization parameters of radiation which has become elliptically polarized upon being reflected from the sample. On the basis of Fresnel's and Airy's equations, usually the refractive index and the thickness is determined. Extending this technique into the infrared range means a possible disadvantage of reduced sensitivity due to longer wavelengths and weak absorptions. At the same time it means the enormous advantage that molecular vibrations are compound specific and their effect depends on molecular orientation and order.

Spectroscopic infrared ellipsometry exploits the facts of obtaining two results per spectroscopic data point, their strictly quantitative interpretation by means of the theory, and the breadth of the simultaneously addressed infrared range. Determining the state of polarization rather than measuring just intensities reduces interference from unwanted contributions e.g. due to scattering, depolarization, or non-ideally flat surfaces. Different from most surface sensitive methods ellipsometry is commonly performed under atmosphere. Basically the method-independent optical constants, i.e. refractive index and absorption index, together with the film's thickness are evaluated. These results serve as reliable basis for any further quantitative interpretation whether related to the vibrational structure or to the geometric model of the system. Presently we are exploring the potential of infrared ellipsometry for anisotropic samples.

In this contribution the experimental technique and evaluation approaches applied in infrared ellipsometry will be outlined. Examples illustrate how to deal with different questions and prove the applicability of infrared ellipsometry to virtually all materials. The outlook will focus on achievements which are expected from the use of synchrotron radiation.

RAMAN INVESTIGATION OF THE KINETICS OF DENSIFICATION PROCESSES IN SILICA GELS WITH CONTROLLED PORE SIZES

PL17

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Porous gels can be stabilized to produce silica which can be used as a host for organic polymers, liquid crystals and metallic ions. Moreover, when densified, these gels possess superior physical and optical properties, including lower thermal expansion coefficients and higher homogeneity.The present work which was devoted to the structural analysis of silica samples containing controlled pore sizes ranging from 25 Å to 270 Å, focussed on the kinetics of densification processes.

Samples were heated at a temperature of 1050 °C for periods varying from 15 seconds to 6 hours. Raman spectra were obtained for each sample. The structural study was based on the evolution of the frequencies, intensities and profiles of certain characterstic bands: the two defect bands, D_1 and D_2 associated with the vibrations of 4- and 3-membered silica rings, respectively; the band around 800 cm^{-1} and the ν(Si-O-Si) band centered at 430 cm^{-1}.

It was observed that densification is accompanied by a sharp decline in intensity of both defect bands and a broadening of the ν(Si-O-Si) band. This result indicates a significant rearrangement of the silica network in favor of larger silica rings. This evolution appears to be the same for all samples, but the kinetics decrease appreciably with an increase in initial pore size.

ABSTRACTS
SHORT PLENARY LECTURES

FS LASER IONISATION OF C_{60}: FROM ABOVE THRESHOLD IONISATION TO STATISTICAL ELECTRON EMISSION AND OBSERVATION OF RYDBERG STATES

SL1

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Fullerenes are very fruitful models for studying the dynamical behaviour of molecular systems with a large number of degrees of freedom. The ionisation behaviour of fullerenes has received considerable attention in the past decade since it is a molecular system that shows long time scale (μs) thermal ionisation that occurs in competition with metastable fragmentation channels and radiative cooling [1]. In a recent series of experiments, that will be described in the talk, we have investigated the ionisation [2] and fragmentation [3] behaviour of C_{60} as a function of the time available for the excitation step using fs-ps pulses from a Ti:Sapphire laser. The pulse duration was varied in the range 25 fs - 5 ps. Photoelectron spectra measured as a function of the laser pulse duration τ showed three distinct ionisation regimes: (I) direct multiphoton ionisation for $\tau < 50$ fs, (II) statistical electron emission for 50 fs $< \tau <$ 1ps leading to thermal electrons with very high temperatures and (III) statistical electron emission with much lower temperatures for $\tau >$ 1ps. Regime (III) is accompanied by a long tail on the positive ion mass spectrum indicating the occurrence of microsecond delayed ionisation and substantial fragmentation. Regime (II) is interpreted as being due to statistical electron emission from the electronic degrees of freedom before coupling to vibrational excitation can occur. Comparison with other experiments and statistical modelling shows that the temperatures extracted from the photoelectron spectra are consistent with the excitation energies needed to produce the corresponding ion mass spectra. The data can provide considerable information on the timescales for energy coupling. In addition, for relatively long pulse durations (ps) when there is sufficient time during the laser pulse for a significant amount of energy relaxation to occur, it is possible to observe Rydberg series in the photoelectron spectra. We appear to be resonantly exciting a superexcited state, observed previously in photoabsorption studies [4]. This state relaxes on the timescale of the laser pulse to lower lying Rydberg states that can subsequently be ionised by one additional photon.

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SL2

ELECTRONIC SPECTRA OF CARBON CHAINS AND THEIR RELEVANCE TO ASTROPHYSICS

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The electronic spectra of neutral carbon chains, their anions and cations are being observed in the gas-phase. Three different approaches are used. The transitions of the chain radicals $C_{2n}H$ n=3-6 and of the bare carbon species C_4 ,C_5 have been detected by cavity ringdown spectroscopy in a slit discharge. The electronic transitions of the polyacetylene and cyanopolyacetylene cations such as $HC_{2n}H^+$ and $HC_{2n}CN^+$ have been measured at high resolution in cell and jet discharges using frequency modulation absorption spectrscopy. Carbon chain anions of the type , C_n^- and C_nH^- have been studied by a two colour resonant photodetachment approach. The gas-phase spectra obtained for the carbon chain species and their ions are compared to astronomical measurements of the diffuse interstellar bands and the implication of the comparisons are considered.

MOLECULAR SPECTROSCOPY IN ASTROPHYSICS: INTERSTELLAR PAHS

SL3

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Polycyclic aromatic hydrocarbons (PAHs) are now considered to be an important and ubiquitous component of the organic material in space. PAHs are found in a large variety of extraterrestrial materials such as interplanetary dust particles (IDPs)

Infrared Space Observatory (ISO) have confirmed the ubiquitous nature of the UIR bands and their carriers. PAHs are thought to form through chemical reactions in the outflow from carbon-rich stars in a process similar to soot formation. Once injected in

A long-term laboratory effort has been undertaken to measure the physical and chemical characteristics of these carbon molecules and their ions under experimental conditions that mimic the interstellar conditions. These measurements require collision-fre ions.

PHOTOCHEMICAL REACTIVITY OF MATRIX ISOLATED MONOMERIC HYDROXYL CONTAINING COMPOUNDS

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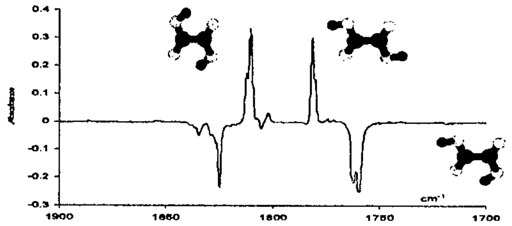
When used together with conventional spectroscopic methods (*e.g.*, FT-IR spectroscopy), matrix isolation constitutes a very convenient technique to undertake photochemical studies on single molecules that are not easily accessible to experiment under other sampling conditions, such as carboxylic acid monomers, which show a strong tendency to aggregate.

Once a matrix of a given substance has been prepared, *in situ* irradiation of the target matrix-isolated molecule at a proper wavelength enables the promotion of different types of photochemical processes which, most of times, can be easily probed spectroscopically. These include conformational interconversions [1,2], tautomerization reactions [3] and fragmentation processes (including photo-degradation reactions) [4].

In this communication results of both electronic and vibrational photochemical studies carried out on a series of different matrix-isolated carboxylic acid monomers will be presented. Besides more conventional techniques, a novel approach based on irradiation at a frequency matching that of the 1st overtone of a particular vibrational mode will be described.



IR difference spectra (6755 cm^{-1} irradiated sample - 6712 cm^{-1} irradiated sample) of oxalic acid monomer isolated in an Ar matrix showing bands due to its 3 lowest energy conformational states.

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ADVANCES IN INFRARED CRYOSOLUTION STUDIES OF WEAK INTERMOLECULAR INTERACTIONS

SL5

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Three aspects of cryosolutions research will be highlighted. The first is the investigation of simultaneous infrared transitions that are detected in binary mixtures. When a molecule A is in sufficiently close contact with a molecule B, the probability that a photon simultaneously excites a vibrational mode in A and one in B is non-zero, which gives rise to a very weak absorption band in the infrared spectrum at the sum frequency of the excited modes. The effect will be illustrated using solutions of CF_3Br in liquid nitrogen. Monte Carlo simulations of these solutions, that were used to verify the theory proposed to predict their intensities [1], will be reported. Preliminary results on liquid O_2/N_2 mixtures will also be reported.

Recent *ab initio* predictions [2] of the "anti-hydrogen bond" characteristics of the complex between fluoroform and dimethylether have drawn a lot of attention. The cryospectroscopy of this type of complexes is the second aspect that will be treated. Results on the fluoroform complex and on complexes between dimethylether and other fluorinated methanes will be discussed, also in light of DFT calculations performed on them.

Finally, the application of cryospectroscopy in the determination of barriers hindering interconversion of conformers will be illustrated. Given that a non-equilibrium mixture of the conformers can be prepared, at sufficiently low temperatures its evolution towards equilibrium can be followed in time. The temperature dependence of this evolution allows the barrier to be determined [3]. This technique will be illustrated in detail using the *cis/trans* conformational equilibrium in methyl nitrite.

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SL6

TRANSIENT ABSORPTION SPECTRA OFTRIPLET STATES AND CHARGE CARRIERS OF CONJUGATED POLYMERS

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The identification of efficent electroluminescence from conjugated organic polymers[1,2] has opened up an exciting area with applications ranging from light emitting diode (LED) displays to polymer lasers. This has been stimulated by the attractive cost and ease of processing of polymer systems, and the first light emitting polymer based display systems are already approaching commercial implementation. The general mechanisms of electroluminescence in these systems are well established, involving generation of positive and negative charge carriers by charge injection from appropriate electrodes, followed by excited state production *via* charge recombination.[3] However, information on the nature of the charge carriers (radical ions) is still limited. We have shown that the positive and negative charge carriers of the polymer MEH-PPV can be prepared efficiently by pulse radiolysis in solutions in chloroform and tetrahydrofuran, respectively, and monitored by transient absorption spectroscopy.[4] We extend these studies to a number of the other commonly used polymers in electroluminescent systems. Spectral and kinetic data on the charge carriers in these systems will be presented, and will be compared with results for monomers and oligomers. The charge recombination reaction responsible for light emission also produces excited triplet states, which are normally non-emitting. Direct photoexcitation of triplet states is spin-forbidden. However, we have shown that these can be efficiently populated in pulse radiolysis experiments by energy transfer from appropriate donors.[5] Spectral and kinetic data will also be presented on triplet states in these systems. In addition, the effect of having more than one triplet excited state on each chain will be discussed and results on intrachain delayed fluorescence presented.

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VIBRATIONAL SPECTROSCOPIC STUDY OF METAL-METAL BONDED COMPLEXES FORMED IN AQUEOUS SOLUTION

SL7

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A great number of metal clusters were studied by infrared and Raman spectroscopy. In most cases less attention has been paid to the complexes in aqueous solution.

A general problem for vibrational spectroscopy from aqueous solution is the lack of observed frequencies. Infrared absorption spectroscopy is restricted to limited window regions because of the strong water absorption. The vibrational bands are broad with a number of unresolved overlapping features. Beside these it is very difficult to obtain Raman spectra in the low frequency region (below 120 cm^{-1}).

The formation of a family of novel oligometallic platinum-tallium cyano complexes with a direct and non-buttressed metal-metal bond has been reported recently [1-3]. Four binuclear complexes can be obtained. The nature of the metal-metal bonds in the binuclear compounds with the general formula $[(NC)_5Pt\text{-}Tl(CN)_n]^{n-}$ (n=0-3) is of special interest. Beside this the above complexes have attracted attention in light-to-energy conversion processes due to the possibility of two-electron transfer reaction between Tl(III) and Pt(II), giving Tl(I) and Pt(IV).

Structural study of the bimetallic complexes (n = 1-3) in aqueous solution has been performed by means of EXAFS technique. The structure of the compound $(NC)_5Pt\text{-}Tl$ (n=0) has been determined by combining results from X-ray powder diffraction (XRD) and EXAFS methods [4].

The Raman spectra of the solutions were measured by means of a Bio-Rad FTS-6000 spectrometer equipped with an FT-Raman accessory. The IR spectra were recorded in CaF_2 windowed cell with a Bio-Rad FTS-375 spectrometer.

Full assignment and full force constant calculations were performed for the above listed four complexes. A reasonable correlation were obtained between Pt-Tl stretching force constants and bond distances for this series of binuclear complexes (Table 1.)

TABLE 1. Pt-Tl stretching frequencies, force constants and bond distances

Molecule	ν(PtTl) [cm^{-1}]	K(PtTl) [Ncm^{-1}]	R(PtTl) [Å]
$[(NC)_5PtTl$	211,195,164,151*	1.651	2.627
$[(NC)_5PtTl(CN)]^{-}$	163.7	1.736	2.598
$[(NC)_5PtTl(CN)]^{2-}$	162.6	1.693	2.618
$[(NC)_5PtTl(CN)_3]^{3-}$	159.1	1.563	2.638

*Solid state splittings of Raman bands

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SL8

DYNAMICS AND MECHANISM OF THE ELECTRON TRANSFER PROCESS OF CYTOCHROME *C* PROBED BY RESONANCE RAMAN AND SURFACE ENHANCED RESONANCE RAMAN SPECTROSCOPY

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Cytochrome *c* (Cyt) acts as an electron carrier in the respiratory chain of aerobic organisms. Despite substantial progress made in the structural analysis of Cyt and its reaction partner, the membrane-bound enzyme cytochrome *c* oxidase (CcO), the mechanism of the interprotein electron transfer is far from being understood. In this respect, resonance Raman (RR) spectroscopic methods promise to contribute to the elucidation of structure-function relationships of these proteins since these techniques selectively probe the vibrational spectra of the heme groups that constitute the redox sites. RR spectroscopic studies have shown that upon binding to CcO, Cyt undergoes a transition from the native state B1 to a conformational state B2 that exhibits an altered heme pocket structure. As the portion of this state B2 formed in the Cyt/CcO complexes correlates with the enzymatic activity of CcO towards Cyt, it was suggested that the interprotein electron transfer is coupled with a conformational B1→B2 transition. In order to test this hypothesis, we have employed an approach which allows a detailed characterization of the redox process of Cyt at a charged electrode that may be taken as a model for the charged binding domain of CcO. We have employed stationary and time-resolved surface enhanced RR spectroscopy that offers the advantage to exclusively probe the heme proteins adsorbed on a silver electrode, thereby providing information both about the thermodynamics and kinetics of the interfacial processes and the heme pocket structures of the species involved. It was found that the structural changes in state B2, which include an exchange of the axial methionine ligand of the heme, are associated with a substantial negative shift of the redox potential as compared to the native B1 state. Whereas the state B2 prevails at more positive potentials, the conformational equilibrium is shifted to B1 upon lowering the potential. Using electrodes coated with self-assembled monolayers of mercapto alkanoic acids which can electrostatically bind Cyt, the portion of state B2 decreases with increasing length of the alkyl chain. These findings imply that the formation of B2 is induced by the electric field in the electrical double layer of the electrode. In order to elucidate the dynamics of the electron transfer reactions and conformational transitions, we have employed time-resolved SERR spectroscopy that probes the interfacial relaxation processes subsequent to a rapid potential jump. On the bare silver electrode, the time scale of the conformational transitions varies sensitively with the potential, i. e., from the second to the short millisecond range. Strikingly small values were determined for the formal heterogeneous rate constants of the adsorbed Cyt and, moreover, these constants were found to be nearly the same for both state B1 and B2 (i. e., ~3 s^{-1}). On the other hand, Cyt bound to a coated electrode prepared with mercapto dodecaonic acid exhibits a much faster electron transfer rate indicating that the strong electric field, that is sensed by Cyt directly attached to the electrode, may substantially slow down the interfacial electron transfer. The implications of these findings for the biological electron transfer process of Cyt will be discussed.

STRUCTURAL CHARACTERIZATION BY NMR OF RIFABUTINOL, A DERIVATIVE OF RIFABUTIN

SL9

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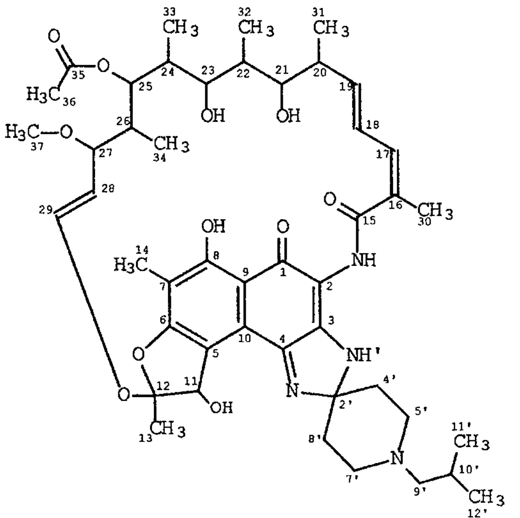
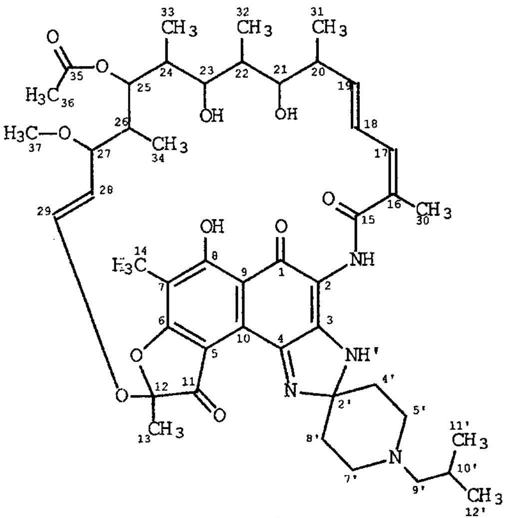
Rifabutin, a naphthalenic ansamycin, is a specific inhibitor of bacterial DNA-directed RNA polymerase and inhibits *in vitro* the replication of HIV-1. The synthesis of rifabutinol by $PtO_2/NaBH_4$ reduction of rifabutin in ethanol is described. Full assignments are presented of the ^1H and ^{13}C NMR chemical shifts using two-dimensional homonuclear and heteronuclear correlation techniques and selective proton decoupling methods. The three-dimensional structure of the ansa-chain of rifabutinol is calculated from NOE-contacts and vicinal coupling constants, using simulated annealing restrained molecular dynamics starting from random coordinates. Measurements of the ^{13}C T_1 relaxation times of rifabutin in solution are consistent with a rigid ansa chain.



Rifabutinol



Rifabutin

SL10

DENSITY FUNCTIONAL THEORY PREDICTION OF POLYCYCLIC AROMATIC HYDROCARBONS VIBRATIONAL SPECTRA

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Density Functional Theory Calculations (B-LYP/ 6;31G) have been performed on different series of polycyclic aromatic hydrocarbons (PAH) with the aim of understanding the evolution of vibrational spectra with increasing the number of condensed aromatic rings in the molecules.

The series of PAH belonging to D_{6h} point group of increasing size (from coronene (C_{24}) to C_{96}) and the series of rylenes (from perylene to quinquarylene) have been considered.

For all these molecules the predicted non resonant Raman spectra are very selective: they show few very strong bands, in excellent agreement with the experimental findings. Theoretical spectra have been indeed compared with the experimental ones recorded for several PAH samples recently synthesised, with known, well-defined structures.

The main aim of this work is to study the rules which determine the intensity behaviour in the Raman spectrum of these compounds: the understanding of this behaviour is in fact of fundamental importance for the interpretation of Raman spectra of several new carbon based materials containing some amount of "graphitic" domains.

Computed Raman intensities of PAH molecules have been discussed in terms of contributions from local displacements by analysis of Raman polar tensors and polarizability derivatives with respect to internal coordinates. Huge variations of the polarizability tensors associated with CC stretching coordinates have been detected; these parameters are clearly correlated in values and sign with molecular symmetry and topology.

The analysis of stretching parameters in the PAH and their evolution with increasing the size of the molecules allow to propose a new interpretation about the origin of the Raman D line observed in disordered graphites and in carbon materials which contain some amount of carbon atoms in sp^2 hybridisation.

CORRELATION BETWEEN UV SPECTRAL AND QUANTUM CHEMICAL CALCULATION DATA ON HETEROCYCLIC MOLECULES

SL11

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A general survey for possible correlation between the U.V.Spectral determined acidity constants (i.e. pK_a values) and quantum chemically calculated Proton Affinities (PA) and/or acidity constant values in gas and liquid phases respectively was done on some five, six membered and fused heterocyclic molecules. In most of the cases a reasonable correlation was obtained. A “Score Hitting Table” was done to determine the most successful method.

SL12

REACTIONS OF UNSATURATED HYDROCARBONS ON METAL SURFACES STUDIED BY RAIRS

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Metal single crystal surfaces are excellent models for elucidation of the nature, geometry and reactivity of adsorbed species. Similar transition metal surfaces often perform quite differently in heterogeneous catalysis, resulting from different bonding of the reagents, intermediates and/or products to the surface. The degree to which a metal perturbs an adsorbate depends on the geometrical arrangement of the surface metal atoms versus the adsorbed molecule and on the availability of a partially filled metal conduction band. Transition metal surfaces like Pt(111) and Ru(0001) have been extensively studied with respect to the adsorption of small molecules such as CO and NO. The chemistry of small alkenes, especially ethylene, on these surfaces, has also been studied by a successful combination of theoretical and experimental methods. In the last few years, this study has been extended to longer alkenes [1] and alkynes [2].

Among the numerous surface techniques available, reflection-absorption infrared spectroscopy (RAIRS) provides very clear information, given the fact that the metal surface selection rule is strictly obeyed. The spectrum shown in Fig. 1 refers to 3-hexyne adsorbed on Ru(0001) at 320 K. It indicates that methylidyne is the only surface species formed, since the 3028 cm^{-1} peak corresponds to the νC-H mode.

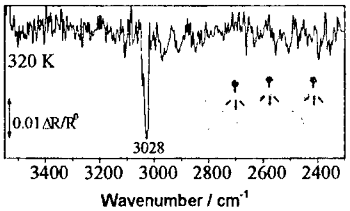

Fig. 1 – Stretching region of the RAIR spectrum of 3-hexyne adsorbed on Ru(0001) at 320 K.

In this work, the adsorption and decomposition of several hexene and hexyne isomers on Ru(0001) are compared, using RAIRS. The reactivity of this surface towards C-H an C-C bond breaking is analysed in comparison to Pt(111).

It is shown that not only the final decomposition products but also the decomposition pathways depend on the chain-length and on the position of the functionality.

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FLUORESCENCE STUDIES OF POLYMER-SURFACTANT ASSOCIATION

SL13

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General aspects of association phenomena in polymer and surfactant solutions, with emphasis of mixed solutions, are outlined and the role of fluorescence as a key approach to unravel molecular mechanisms is reviewed.

Fluorescence techniques have been central in probing polarity, for determining the size of micelles and microemulsion droplets, to distinguish between intra- and inter-association of polymers and for monitoring conformational changes of polymers.

Fluorescence spectroscopy has been successfully used to investigate the association of water-soluble polymers to which have been grafted hydrophobic fluorphores; these will be intrinsic probes of hydrophobic association. With hydrophobically modified poly(acrylate) we have investigated the effect of solvent polarity as well as pH and also the coassociation with cationic surfactants.

Fluorescence microscopy can be used to probe conformational changes of high molecular weight polymers, in particular DNA; these conformational changes are a central issue in gene delivery where DNA compaction is believed to play a critical role. The compaction of DNA by cationic surfactants has been investigated and is found to depend strongly on surfactant alkyl chain length. In mixed systems of cationic and anionic surfactants, compaction/decompaction can be followed as the surfactant mixing ratio is varied. Furthermore, compaction of DNA on the surface of thermodynamically stable catanionic vesicles has been demonstrated.

SL14

LINKING UP TWO SPECTROSCOPIC TECHNIQUES TO SOLVE AN ANALYTICAL PROBLEM: DEGREE OF ACETYLATION OF CHITIN AND CHITOSAN

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Chitin and its deacetylated derivative chitosan are interesting biopolymers with a constantly increasing number of applications in a variety of fields. Despite the specific designations of poly-N-acetyl-D-glucosamine for chitin and poly-D-glucosamine for chitosan, these terms actually correspond to a family of polymers varying in the acetyl content measured by the degree of N-acetylation (DA). Since the DA dictates the behaviour of these polymers, namely reactivity and solubility, the accurate determination of that quantity has been one of the major concerns over many decades. The difficulty of determining the DA is well illustrated by the extensive number of different techniques, either modern instrumental or classic, which have been used for this purpose and frequently yield to different values.

^{13}C CP/MAS NMR spectroscopy is one of the most powerful techniques allowing a direct determination of the DA of both soluble and non-soluble samples and requiring non-specific sample preparation. However, due to its high cost and complexity that technique will hardly be used for routine determinations. So, we have chosen the ^{13}C CP/MAS NMR spectroscopy to calibrate the non-direct, but user-friendly and less expensive FTIR spectroscopy, which has been widely used to determine the DA of those polymers.

In the IR technique the DA is determined using a ratio of the absorbances of a probe band (PB) relative to a reference band (RB), A_{PB}/A_{RB}, measured by the baseline (BL) method. Due to the complexity of the IR spectra of chitin a great number of combinations of A_{PB}/A_{RB} ratios and (BL) have been proposed so far. In this paper we present an improved method to determine the DA by FTIR, based on a statistical evaluation of the ratios $A_{PB(BL)}/A_{RB(BL)}$ resulting from the combinations of all the PB, RB and BL previously proposed and using the ^{13}C CP/MAS NMR spectroscopy as the standard technique[1], after optimisation of the parameters which determine its analytical reliability[2].

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ABSTRACTS
ORAL CONTRIBUTIONS - A

(3s,n) RYDBERG EXCITATION OF JET-COOLED ACETALDEHYDE: A REMPI STUDY USING TWO LASER BEAMS

OA1

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The spectra, photophysics and photochemistry of acetaldehyde have been and remain subjects of continual investigation. The $^1A'(3s \leftarrow n)^1A'$ Rydberg transition, origin at 6.822 eV, has the strongest two-photon signal among the molecules [1]. The (2+1) REMPI spectra, with laser light in the wavelength region of 360 nm is known [1]. The I.P. of acetaldehyde is 10.2 eV. In the present study we tried to detect the (3s,n) transition as a three-photon resonance [(3+2) REMPI] using green laser light (wavelength region 545 nm) focused by an f = 15 cm or f = 25 cm lens. No REMPI signal was detectable in the TOF mass spectrometer. A pulsed jet beam of CH_3COH+He was used. Next, using the above mentioned green laser light (pulse duration ~5 ns, pulse energy ~1 mJ) and its second harmonic UV beam (pulse energy ~ 70 microJ, generated by a BBOI crystal), mass resolved (3s,n) REMPI spectra have been recorded. The REMPI signals are due to the ions: m/z 44 (parent), m/z 29 (HCO^+) and m/z 15 (CH_3^+). The relative intensity of these ions is almost the same. The recorded spectra resemble the (3s,n) two-photon (360 nm) jet-cooled spectra of the literature. An interesting feature is that the m/z 43 ion (CH_3CO^+) has intensity not due to (3s,n) REMPI. The m/z 43 intensity is about half of the parent ion. The experiment shows that the UV light (272.5 nm) dissociates the acetaldehyde molecule to CH_3CO + H and CH_3CO^+ is created by absorption of further photons. By using laser light in the 360 nm region (linear polarized and circularly polarized), we find that the (2+1) REMPI signals are due to m/z = 44, 43, 29, 16, 15 and 14 ions. These results are in complete agreement with the REMPI results obtained by using a quadrupole mass filter [1]. On the contrary, FT-ICR detection of REMPI, did not detect the m/z = 16, 15, and 14 ions [2]. It seems that the presence of a magnetic field [2] affects the dissociation dynamics.

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OA2

AXIAL AND EQUATORIAL HYDROGEN BONDS IN GAS PHASE

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An important type of hydrogen bond dimer B···HX (where X=F, Cl, etc.) is that in which the proton acceptor B carries two non-equivalent lone electron pairs. These non-equivalent binding sites would give rise in some ring molecules to two different axial and equatorial forms when hydrogen bond dimers are formed. We recently reported the first experimental observation of axial and equatorial hydrogen bonds in the heterodimers pentamethylene oxide···HCl [1] and pentamethylene sulphide···HCl [2]. Such studies have been undertaken in the collisionless environment of supersonic jets where complexes are formed and can be probed using Fourier transform microwave spectroscopy. In this contribution we present the results on related complexes.

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LOW-FREQUENCY RAMAN SCATTERING FROM GLASSY AND SUPERCOOLED LIQUID BENZOPHENONE

OA3

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We report the first investigation of the low-frequency Raman scattering from both glassy and supercooled liquid benzophenone in the wide temperature range from 10 to 350 K with glass transition temperature at 212 K.

Three bands were observed in glassy benzophenene that are absent in the Raman spectra from crystalline benzophenone. In the low temperature region (T<200 K) two bands have been seen around 20 cm^{-1} and 100 cm^{-1}. The former is the so-called Boson peak (vibrational contributions) [1] and the latter is attributed to the molecular motions, which corresponds to librational optical phonons.

For temperatures close to the glass transition temperature Boson peak is hidden under the envelope of a significantly broadened quasielastic line, which is usually referred to some kind of relaxational motion [2]. The temperature evolution of a low frequency modes have been discussed in the framework of the existing models.

In addition, the process of crystallization from the melt at the temperature 225 K have been observed. It should be noted, that the formation of the crystalline phase is so much slow process that we have not seen any thermal anomaly in the region 225 – 240 K from the differential scanning calorimeter analysis at a temperatute increasing rate of 10 K/min.

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OA4

SPECTROSCOPIC STRUCTURAL STUDY OF THE R2 REPETITION OF THE C-MYB TRANSCRIPTION FACTOR

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c-myb is a protooncogene involved both in the proliferation and the differenciation of hematopoietic cells from various lineages (human, chicken, mouse...). The protooncogene product is a transcription factor (c-Myb) which stimulates target genes expression by binding to DNA. It takes place near the N terminal extremity in the DNA binding domain, which domain contains 3 imperfect repetitions, of about 50 amino acid residues each, arranged in tandem (named R1, R2, R3). R2 and R3 then form a double helix-turn-helix (HTH) super-secondary motive, which docks into the major groove of DNA when c-Myb is bound.

In order to understand more how this interaction occurs, we focused our attention to the R2 repetition at the molecular level without presence of DNA. We shown by using circular dichroism spectroscopy, that R2 is made of 56 % of α helix, and 44 % of undefined (turns + random coil) conformations in standard conditions (no strand are observed at all). Furthermore, we localised these structures along the sequence by using the LINK method[1], which combines theoretical predictions with experimental spectroscopic data : R2 contains 3 α helices ($\alpha 1$, $\alpha 2$ and $\alpha 3$) but the last one seems to be less stable (more flexible) than the two others. Therefore, we propose that this unstable region fold into an α helix only when c-Myb binds to DNA, which confirms the hypothesis proposed by some authors.

We also have probed the effect of different solvents, at different concentrations, on the cooperativity of the helices contained in the secondary structure of R2. We conclude that methanol seems to structure R2 and can mimic the effect of other helices. Finally, we looked for the presence of β turns by using prediction methods, in order to determine the orientation of the α helices.

All the obtained results bring new arguments onto the hypothesis of a conformational transition between c- Myb free and c-Myb bound to DNA : the flexible region, C-terminal part of R2, folds into a third helix and gives an helix-turn-helix motive upon complexation.

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INVESTIGATION OF SKIN CANCERS BY FT-IR SPECTROSCOPY

OA5

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What distinguishes a pathological tissue from a normal one, is essentially the clear change in the cellular biochemistry. Therefore many efforts have been made to improve early diagnostic and prognostic methods in order to better understand the biological nature of the diseases. Nowadays the high resolution techniques allow to adopt a global approach to the investigation of the initial stages of the transformation processes due to a pathology, suggesting new more reliable experiments.

Among the several methods, recently employed for the diagnosis of disease states in the medical and/or pharmacological field vibrational spectroscopy have been particularly and successfully applied, due to the possibility to perform quantitative analysis on the different chemical compositions and molecular structures of healthy and pathological tissues. Recently Fourier Transform Infrared absorption (FT-IR) spectroscopy has been extensively employed in this field in order to obtain indications about the structural and chemical/physical properties at molecular level. Generally in this field the diagnosis is performed by means of invasive techniques based on the removal of a part of the tissue, which can themselves contribute to the progression of the cancer, so the possibility to perform a diagnosis in vivo by a non-invasive technique and in real time, such as spectroscopic methods, can become really important.

In this work we report a detailed study of Fourier Transform Infrared spectroscopy on normal and neoplastic human skin samples suffering two kinds of cancers, namely epithelioma and basalioma. The analysed skin samples have been drawn from different parts of the human body, after biopsies. By performing a complex bands deconvolution due to the complexity of the tissue composition, the experimental analysis, in the considered frequency region (900 - 4000) cm^{-1} of the collected IR spectra, allowed us, first of all, to characterize the two different kinds of cancers and showed clear different features passing from the normal tissue to the malignant one in particular in the region from 1200 cm^{-1} to 2000 cm^{-1}, typical of the lipids bands.

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OA6

FLUORESCENCE PROPERTIES OF LOW-CONCENTRATED PORPHYRIN SOLUTIONS

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This contribution presents fluorescence measurements of porphyrin solutions. The molecules were dissolved in acetone and fluorescence signals could be achieved from solutions whose concentrations ranged from 10^{-8} to 10^{-18} M. The laser-induced emissions were detected by a Raman spectrometer (Jarrell-Ash 25-400; double monochromator, 1m focal length, photon counting system with 16 bit resolution) whose false light is negligible. The samples were placed into a spinning cell. In determining the concentration at the chosen detection limit (10^{-18} M), the maximum total error has been estimated to 45%.

For the attomolar solution, the signal-to-noise ratio of the S_0-S_1 transition amounts 3.2:1 (Fig. 1a). This transition is attributed to monomeric species and an overall photon balance-sheet gives an estimation how many molecules do contribute to the signal during measuring cycles. Within the dilution series, the S_1-S_0 fluorescence shows a definite non-linear dependence on the chosen concentration. Picomolar as well as femtomolar solutions exhibit strong blue-shifted fluorescence emissions (Fig. 1b).

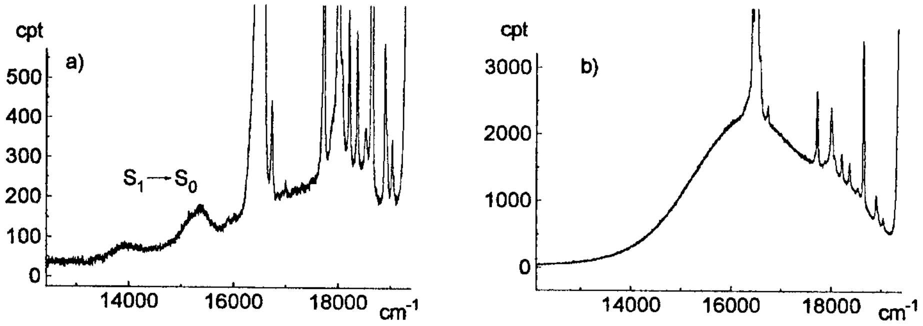

Fig.1 : fluorescence spectra of porphyrin solutions; 1a: 10^{-18} M; 1b: 10^{-13} M; the S_1-S_0 (0-0) transition is located at 15370 cm^{-1}; Fig 1b depicts time-stationary fluorescence; the peak-like emissions are Raman signals of the solvent; cpt: counts per detection time for each measuring step

These bands are time-stationary as well as non-time-stationary. Their origin is attributed to the formations of aggregates both in the ground state and in electronically excited states. The spectral feature is discussed in comparison to spectra of aggregated carotenoporphyrin molecules and porphyrin assemblies, which were dissolved in solvent mixtures.

CALCULATION OF SPECTROSCOPIC CONSTANTS USING NEURAL NETWORKS

OA7

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Neural networks are becoming powerful tools for researchers in many fields. Problems of pattern recognition, classification, modeling, association and mapping are often treated more successfully with neural networks than with classical mathematical methods. Within chemistry it has been shown to solve a wide range of problems [1]. Neural networks are rather simple computer programs where neurons are processing elements that are connected in nets that can receive and transmit information among themselves. The input received by a processing element is processed through a transfer function and then transferred to other processing elements. The transferring process is modified by different weights. It is the adjustment of the weights that enables the network to learn and become a model for the actual problem.

The purpose of the present work is the predictions of several molecular properties, based on input information of a few different molecular properties. We consider the diatomic hydrides from LiH to HBr, altogether 21 molecules. The spectroscopic constants under investigation are the equilibrium distance, four vib-rot constants, the dissociation energy and the frequency of the first electronic transition, the values of which are given by Herzberg [2]. As input parameter we chose the equilibrium distance and the atomic number of the heaviest element, leaving us with six output values to predict. A problem of this kind requires supervised learning, and a neural network using back propagation is suitable. It turns out that six rather small networks with one hidden layer gives good accuracy. The results are analyzed with statistical scores for both the training, test and validation sets. The results are also compared with - and found superior to - classical mathematical methods.

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OA8

THEORETICAL DETERMINATION OF NUCLEAR QUADRUPOLE COUPLING CONSTANTS

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Density functional calculations of electric field gradient tensor at the nitrogen, oxygen,boron and lithium nuclei, in a series of test molecules, have been performed using the linear combination of Gaussian-type orbital Kohn-Sham density functional theory (LCGTO-KS-DFT) approach. Local and gradient corrected functionals were used for all-electron calculations. All molecular structures were optimised at their respectively levels of theory with extended basis sets. 14N,17O,11B and 7Li calibrated nuclear quadrupole moments were obtained. With these calibrated nuclear quadrupole moments, the nuclear quadrupole coupling constants of a series of organic and inorganic systems were determined. The selected applications concern:

- XNC/XCN (X=B,Al,Ga,In,Li,Na,K,Rb);
- Fluorometylisonitrile, pyridine, pyrazine, pyrrole,1,8-Bis(dimethyl-amino naphthalene;
- beta-HMX, cocaine and heroin;
- benzoyl fluoride, phthalimide;
- phthalic anhydride, maleic ahydride;
- p-chlorobenzaldehyde,p/m-nitrobenzaldhehyde;
- LiNaF2

The excellent agreement between the calculated and experimental data encourage the extention of the work to other quadrupole nuclei of chemical interest. These studies are currently in progress in our laboratory.

A NEW APPROACH TO CONSTRAINED MOLECULAR DYNAMICS

OA9

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So far the only constraints explicitly considered in molecular dynamics are those imposed to interatomic distances while the more flexible approach adopted here considers on equal footing distances, valence angles and torsions defined in ref. (1). The treatment relies on a basis change by which a complete set of molecular displacements is defined, whose metric tensor factorizes in two blocks, one for the constrained subset and the other for all remaining, unconstrained coordinates.

An expansion of the constrained Cartesian displacements is thus obtained, which may be extended to any order and is explicitly written up to the second order, compatible with a simple integration algorithm containing only the acceleration. It turns out that a numerical implementation of the final equation requires a linear transformation, from Cartesian to molecular coordinates, which must be defined only for the members of the constrained subset.

This geometrical approach reduces the number of degrees of freedom of a constrained system while all precedent works, see the recent articles (2) and (3), dispense with the elimination of the surplus variables adding a set of auxiliary conditions and the undetermined Lagrange multipliers. The latter are not used in the present treatment although they may be calculated, if one so wishes, from the final expression of the constrained Cartesian displacements.

It is found that all precedent equations for the constrained motion suffer of an inconsistent derivation and include unnecessary calculation at each time step, in the iterative procedure required to satisfy the constraints with the desired accuracy. It is actually shown that the very definition of the Lagrange multipliers must be reconsidered as they produce, in the general version ref. 3, constraint forces not normal to the surface of the constraints. A further point of difference is relative to the constrained momenta, which identically vanish under the chosen constraints in the present formulation while this property is not possessed by quantities previously introduced (4) under the same name.

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ABSTRACTS
ORAL CONTRIBUTIONS - B

CONFORMATIONAL STUDIES OF MONOSUBSTITUTED THREE-MEMBER RINGS BY VARIABLE TEMPERATURE FT-IR SPECTRA OF RARE GAS SOLUTIONS

OB1

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The conformational stability of cyanomethylcyclopropane (the cyano group is frequently considered a pseudohalogen) was initially determined [1] experimentally in the liquid phase with the *gauche* form proposed to have 87% abundance at ambient temperature but the stability in the liquid may not be the same as that in the gas phase. Thus, we recently carried out a conformational study of cyanomethylcyclopropane by investigation of the variable temperature infrared spectra of this molecule dissolved in liquid xenon. These studies gave an enthalpy difference of 54±4 cm^{-1} (0.65±0.05 kJ/mol) with the *gauche* conformer the more stable form where the estimated amount of this rotamer is 72% at ambient temperature.

We have also investigated the vibrational spectra of cyclopropylmethylacetylene (ethynylmethylcyclopropane) $c\text{-}C_3H_5CH_2CCH$. There had been a conformational study of this molecule from the microwave investigation as well as from *ab initio* calculations [2]. It was concluded that the *cis* conformer was more stable than the *gauche* rotamer by 64±30 (0.77±0.36 kJ/mol) from relative intensity measures in the microwave transitions. This result is in contrast to the *ab initio* calculations at the RHF/6-31G(d) level which predict the *gauche* conformer more stable by 132 cm^{-1} (1.58 kJ/mol) and the electron diffraction investigation which indicated that the *gauche* rotamer was more stable by 152±45 cm^{-1} (1.82±0.54 kJ/mol). We have carried out infrared and Raman spectral studies of the fluid and solid states as well as an investigation of variable temperature mid-infrared study of xenon solutions of this molecule. Additionally, we performed *ab initio* calculations with much larger basis sets than were previously used [2] with full electron correlation by the perturbation method to the second order. The results of this spectroscopic and theoretical study as well as some more recent investigations of the conformational stability of fluoromethylcyclopropane will be reported.

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OB2

FTIR STUDIES ON THE VIBRATIONAL FUNDAMENTALS OF NOVEL CLUSTERS OF Ge AND C TRAPPED IN Ar

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Previous studies in this laboratory, which combined Fourier transform infrared (FTIR) measurements in solid Ar with density functional theory (DFT) calculations, proved particularly productive in identifying the vibrational modes and determining the structures of novel clusters of silicon and carbon.[1,2] We report here the early results of investigations of two new groups of species for which no theoretical predictions or measurements of vibrational fundamentals have so far been reported: mixed clusters of germanium and carbon and pure germanium clusters.

Both Ge_n and Ge_nC_m clusters are produced by trapping the products from the Nd-YAG laser evaporation of germanium and carbon rods in solid Ar at 10 K. Using the high natural abundance of several Ge isotopes and appropriate ^{13}C enrichment of the carbon rod, isotopic shifts have been measured and compared with the predictions of DFT theory using various functionals. Agreement between theoretical calculations and experimental measurements is very good. Comparisons with earlier results for the structures and vibrations of mixed Si_nC_m and pure Si_n clusters will be discussed.

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FTIR SPECTROSCOPIC CHARACTERIZATION OF BIOMATERIALS USED TO BONE RECONSTRUCTION

OB3

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FTIR spectroscopy has been used to analyze the process of mandibular bone rabbit reconstruction taking place in the presence of various implant materials. Two types of implants materials differing in their surface properties have been examined: oxidized carbon fabrics and carbon fabrics coated with pyrolitic carbon. For comparison natural bone reconstruction (without any implant material) has been studied. Samples of the bone for the studies have been withdrawn at different time intervals after implantation. The ratio of bone components has calculated from the FTIR spectra of the samples basing on the integrated areas of the bands due to phosphates (900-1200 cm^{-1}) and amide (1400-1700 cm^{-1}). Additionally analysis of the shape and intensity of these bands has provided information on the course and the progress of bone mineralization process. The complex band envelopes have been numerically deconvoluted into components.

The investigation has shown that osteointegration process is faster in the presence of the carbon fabrics with pyrolitic carbon used as an implant material. Obtained results indicate that FTIR spectroscopy is a useful tool which may complete histopatological examinations. FTIR studies make it possible to select implant materials used to substitute natural bone tissue.

OB4

DIAGNOSIS OF PEPTIC ULCER IN HUMANS THROUGH LASER BASED BREATH ANALYSIS.

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A Tunable Diode Laser Absorption Spectroscopy (TDLAS) system for medical diagnostics has been realised at the ENEA High Resolution Molecular Spectroscopy Laboratory. This apparatus has been developed for high precision measurements of the isotopic ratio $^{13}CO_2$ /$^{12}CO_2$ in the expired human breath for the diagnosis of Helicobacter pylori infection in the human stomach, which is considered to be responsible for peptic ulcer. The decomposition of urea (in our diagnosis marked with ^{13}C) by H. pylori in patients suffering from peptic ulcer is causing a significant increase of the $^{13}CO_2$ concentration (about 5 %) with respect to $^{12}CO_2$ in human breath.

The TDLAS system is based on a 4.33 μm diode operated slightly above liquid nitrogen temperature. The collimated multimode mode laser emission is directed into a White type multipass cell (2 m optical path) filled with the gaseous sample under analysis. A 50 cm focal length Czerny -Turner monochromator operating with a 150 grooves/mm grating is used for mode selection. The transmitted single mode laser beam is focused onto a HgCdTe detector by an off-axis parabolic mirror and averaged on a digital oscilloscope (Tektronix 2430) and subsequently transferred to a PC through a GPIB interface.

A dedicated software written in Quick-Basic (BREATH.BAS) performs data-acquisition, wavelength-linearization of the spectra and further analysis, including calculation of the absorbance, and fitting the selected absorption lines to Gaussian line profiles in order to obtain the relative $^{13}CO_2$ /$^{12}CO_2$ concentration.

Particular care has been taken to choose a opportune spectral interval for what concerns the relative intensities of the $^{13}CO_2$ and $^{12}CO_2$ lines as well as their temperature dependence, using the Hitran data base.

Here we present preliminary results, including a discussion of possible experimental errors in the $^{13}CO_2$ /$^{12}CO_2$ ratio determination, the reproducibility of the analysis on samples with a natural $^{13}CO_2$ /$^{12}CO_2$ composition and future developments.

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* ENEA guest

PRESENCE AND PERSPECTIVES OF SURFACE ENHANCED RAMAN SCATTERING APPLIED TO MEDICAL AND ENVIRONMENTAL SAMPLES OB5

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Surface enhanced Raman scattering (SERS) was recently turned into a new attractive light since it was applied to single molecule evidence [1-3]. Optimization of the nanometric surface preparation allowed SERS single molecule studies of a broader range of biosystems, like hemoproteins, nucleotides, or dye-labeled compounds of industrial or environmental interest. In this overview several areas of work are covered. First, there are pointed out the latest approaches of surface enhanced Raman scattering (SERS) with the emphasis on the new possibilities of single molecule detection (SMD) in different biologic or environmental samples. What consequences could this results provide in a large area of genetics, biophysics, trials, new technologies, etc, are subject of enhanced discussions. Secondly, our results from SERS studies of biological samples like human blood and its components are presented. Advantages like high selectivity and fluorescence quenching combined with the confocal Raman or imaging techniques allowed also getting insight into the size-dependent properties of single nanostructure or semiconductor nanocrystals. Further, some of our SERS measurements on natural compounds including those that exhibit potential antitumor or HIV-inhibitor activity are discussed. Example given here is the betulinic acid (BA), isolated from the leaves of Syzigium claviflorum, a compound found to be inhibitor of HIV replication in H9 lymphocyte cells [4]. This new class of inhibitors of human immunodeficiency virus type 1 (HIV-1) was subject of mechanistic studies, revealing an interference with the HIV-1 entry in the cells at a post-binding step. However, the mechanisms were not completely understood [4,5]. The presence of the ν_s(COO) mode in the SERS spectrum of BA suggests a chemisorption of the steroid on the surface [6]. Advantages of the multichannel detection with long acquisition time were further explored here.

Some of the SERS topics with great promise like those covering structural and binding aspects of DNA, labelled proteins, receptor functions in relation to biochemical phenomena, the diversity of systems covered by the term "supramolecular" and their remarkable selectivity towards guests, surface-enhanced Raman optical data storage (SERODS) systems, are finally discussed.

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OB6

CYCLIC PEPTIDES AND THEIR INTERACTION WITH PEPTIDE COATED SURFACES

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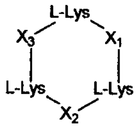
After the antibiotic Gramicidin S was identified as a cyclic decapeptide in 1947, other cyclic active principles have been found [1]. Even today the design and synthesis of a receptor and a target peptide which recognize each other present a difficult problem. Combinatorial chemistry is the common way of synthesis [2]. For a direct approach of the design, some questions must be answered: Which are the functional groups mostly involved in an interaction? Do the water molecules of the solvent strengthen or weaken the bonding? Do the conformation of the cyclic peptides effects the binding mechanism? There are different ways of obtaining the information required. This study presents two of them, one is ATR-FTIR-spectroscopy [3] and another generating computational models. The investigated cyclic hexapeptides have a common leading structure, which consists of three alternating L-Lysine. The other three alternatives in the template are occupied by different L-amino acids (Fig. 1).



X_1	X_2	X_3
L-Phe(pNO$_2$)	L-Phe(pNO$_2$)	L-Phe(pNO$_2$)
L-Phe(pNO$_2$)	L-Phe(pNO$_2$)	L-Arg
L-Phe(pNO$_2$)	L-Leu	L-Leu
L-Gln	L-Gln	L-Gln
L-Glu	L-Glu	L-Glu
L-Ala	L-Ala	L-Ala
L-Leu	L-Leu	L-Leu

Fig. 1 – Cyclopeptides: Combinations of X_1, X_2 and X_3

The silicon ATR-crystal was coated by silanisation and covalent binding of a spacer and the amino acid (R) or the tripeptides (aDS; SDa). The crystal was placed in a liquid measurement cell which was installed to a vacuum FTIR-spectrometer (Bruker IFS 66v). Spectra of the bonded cyclic peptides in these surfaces in correlation with reference surfaces provide information about the participation of functional groups (such as COO^-, NH_3^+, and the amidefunction). Characterization of other bonding behavior is likewise possible. The surface spectra contain features about the interacting groups of both receptor and target molecule. The spectral data (1800 cm^{-1} – 1500 cm^{-1}) are interpreted by band analysis. Assembling the investigated bonding characteristics and computational models detailed conceptions of the molecular interactions can be devised.

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OB7

PREDICTING A QUANTUM MECHANICAL CORRECTION FROM INFRARED INTENSITY PARAMETERS TO MULLIKEN ATOMIC CHARGES

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In the last years, we have shown that a quantum mechanical correction to Mulliken atomic charge can be provided by a particular element of the overlap tensor obtained from the charge-charge flux-overlap model for infrared intensities [1]. The corrected charges reproduce the molecular dipole moment, which is not the case for the Mulliken net charges. Furthermore, these corrected charges have shown to be useful in interpreting adequately inter- and intra-molecular interactions. This overlap term for hydrogen atoms has revealed that its sign can be used to classify various types of interactions [2]. For example, we have seen that this overlap term is small for hydrogen atoms bounded to *sp* carbons with respect to the value of the hydrogen Mulliken charge; on the other hand, it is large for hydrogen atoms bounded to sp^2 or sp^3 carbons. However, it is positive for sp^2 carbons and negative for sp^3 carbons. In this work, we show that this correction ($\Delta^{\sigma\sigma}_{ov,H}$) can be predicted for hydrogen atoms bounded to sp^2 or sp^3 carbons by "atomic additive contributions" obtained from pattern molecules using a RHF/6-31G** calculation. Here σ is the Cartesian axis perpendicular to the molecular plane for planar molecules or to a local symmetry plane for other cases. The considered molecular systems were both halogenated ethylenes and mehtylenes. Two statements were employed to predicted the $\Delta^{\sigma\sigma}_{ov,H}$ values in halogenated ethylenes: i) the contribution to $\Delta^{\sigma\sigma}_{ov,H}$ in ethylene comes essentially from the C=C group; others hydrogen atoms do not contribute to it. (ii) the contribution by the C=C group to any hydrogen atom in halogenated ethylenes is still the same as in ethylene and hydrogen atoms do not contribute as well. On the other hand, the contribution of halogen atom depends on the position of the hydrogen atom with respect to it. The model molecule chosen for evaluating the different contributions of halogen to hydrogens in α, β^{trans} and β^{cis} positions was C_2H_3X. with X= F or Cl.

The obtained results for cis-$C_2H_2X_2$, vic-$C_2H_2X_2$, C_2HX_3, trans- $C_2H_2X_2$, $HCClF_2$, $HCCl_2F$, $HCCl_3$ and HCF_3 show an excellent agreement between the calculated and predicted values for $\Delta^{\sigma\sigma}_{ov,H}$. The rms error was only 0.007.

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OB8

HIGH LEVEL AB INITIO QUANTUM CHEMICAL PREDICTIONS OF INFRARED INFRARED INTENSITIES

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Vibrational intensities in the infrared spectra of H_2O, C_2H_2, HCN, H_2CO, CH_4 and SiH_4 were theoretically predicted by applying *ab initio* quantum chemical methods at different levels of theory. The self-consistent field (SCF), second order Moller-Plesset perturbation method (MP2), configuration interaction with single and double excitations (CISD), quadratic configuration interaction including single and double excitations (QCISD), double excitations coupled-cluster (CCD), coupled-cluster with single and double excitations (CCSD), and coupled-cluster with perturbative triple excitations [CCSD(T)] levels of theory were applied. The atomic orbitals basis sets employed included double-ζ (DZ), triple-ζ (TZ), DZ plus single polarization(DZP), TZ plus double polarization (TZ2P), TZ plus triple polarization (TZ3P), TZ3P augmented with one set of higher angular momentum functions [TZ3P(f,d)], TZ3P augmented with two sets of higher angular momentum functions [TZ3P(2d,2f)], split valence plus polarization [6-311G(d,p) and 6-311G(3d,3p)], split valence with added polarization and diffuse functions [6-311++G(d,p) and 6-311++G(3d,3p)], Dunning's correlation consistent polarized valence [cc-pVXZ (X=2-5)] basis sets as well as augmented correlation consistent polarized valence [aug-cc-pVXZ (X=2-5)] basis sets. The theoretically estimated at the different levels of theory infrared intensities for the studied molecules were compared with available experimental data. For completeness of the analysis the predicted equilibrium geometries, dipole moments and harmonic vibrational frequencies were also compared with experiment. Several highly correlated types of wave functions employing extended basis sets produce intensity values in very good agreement with experiment. The best overall agreement between theory and experiment for all properties studied was obtained from highly correlated wave functions [QCISD, CCSD, CCSD(T)] combined with the Dunning's aug-cc-pVXZ (X=3-5) basis sets.

VIBRATIONAL ANHARMONICITY AND SCALING THE QUANTUM MECHANICAL MOLECULAR FORCE FIELD

OB9

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The interrelationship between the scale factors obtained using Pulay's method [1-4] from the anharmonic and the harmonized vibrational frequencies of a light molecule and its heavy analogue is considered in terms of a Morse potential. The determination of the scale factors from the vibrational frequencies of a light molecule is shown to result in smaller deviations of the calculated and experimental vibrational frequencies of its heavy analogue than those of the reverse procedure. In this context the extent to which Dennison's rule [5, 6] is satisfied is also discussed.

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ABSTRACTS
ORAL CONTRIBUTIONS - C

PHOTOIONISATION AND ABSORPTION METHODS FOR THE INVESTIGATION OF UNSTABLE MOLECULES IN THE GAS PHASE

OC1

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Single and multiphoton ionisation methods in the form of ultraviolet photoelectron spectroscopy (UPS), and resonance enhanced multiphoton ionisation (REMPI) with ion and electron detection are used for the investigation of transient/unstable molecules produced either by on-line methods or by photodissociation of suitable precursors. In combination with infrared absorption, the sought properties of the unstable molecules are details of their ground, excited and ionic states, *e.g.* transition energies, geometric and electronic structure and vibrational frequencies.

Accompanying the experimental investigations are predictions and interpretations based on electronic structure calculations employing both conventional *ab initio* methods and density functional theory.

Examples will focus on the generation and spectroscopy of unstable multiply bonded compounds of boron (BO, BN containing molecules) and novel reactive species containing pseudohalide groups (-OCN, -CNO) and on the multiphoton ionisation of unstable boron and halogen containing diatomics produced by photodissociation processes.

OC2

SPECTRAL INVESTIGATION OF THE SLOW ELECTRON INTERACTION WITH BIOMOLECULES IN GAS PHASE

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The nucleic acid bases are an important component of the genetic structures. For this reason they determine the general physical and biological properties of the nucleic acid molecules. Therefore, the study of slow electron collisions with bases is of particular interest not only for physics, but also in biophysical and radiobiological applications. First of all, these investigations allow one to obtain an information on the intersystem crossing with the formation of the triplet metastable states, which play an important role in many biological processes.

There we report on the results of spectral and mass-spectrometric studies of pyrimidine derivatives of nucleic acid bases: cytosine, methylcytosine molecules. The studies of the puryne derivatives of bases have been described in [1].

Investigations were carried out by a crossed electron and molecular beam method with photoelectric registration of radiation. The research of molecules in gas-phase makes it possible to select the direct processes and to exclude the medium influence. The experimental setup consists of such principal components as: molecular and electron beam sources, collisions chamber, vacuum system, photon and ion detection system. The molecular beam was obtained by means of a special microchannel source, the electron beam – by means of a five–electrode electron gun with warming up oxide cathode. The energy of the monoenergetic electron beam was varied in the 0-300 eV range at energy spray of 0.7 eV.

Electron impact excitation of the cytosine and methylcytosine molecules and their dissociative products were studied by the observation of the fluorescense emission in the spectral range 200-600 nm. Seven spectral bands were observed at electron energy 70 eV The short-wave spectral bands were found to be the most intensive components (λ_m = 290.6 nm for the cytosine and λ_m = 279.8 nm for the methylcytosine, respectively). Other bands have maximum at 328.3; 356.7; 370.9; 392.2; 415.5; 429.3 nm.

The exitation functions (the energy dependences of the relative excitation cross section) of the molecules were measured in the electron energy range from the threshold up to 300 eV. The analysis of the excitation functions in the Bete-Born approximation with the application of the Fano dependences showed the presence of the intersystem crossing with the formation of the triplet molecular metastable states.

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GAS-PHASE ^{17}O AND ^{33}S NMR SPECTROSCOPY

OC3

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Oxygen and sulfur are difficult elements for NMR studies, since their only magnetic nuclei (^{17}O and ^{33}S) have small natural abundance (0.038 and 0.76%, respectively) and both the nuclei have an electric quadrupole moment. The chemical importance of oxygen in organic chemistry has led to considerable interest in the ^{17}O NMR spectroscopy [1]. Hundreds of compounds have been also examined applying ^{33}S NMR spectra. Meanwhile our knowledge on medium effects in the oxygen and sulfur NMR spectra is limited to qualitative estimations and only few single ^{17}O measurements have been previously performed in the gas phase [2,3]. Gas-phase NMR spectra are important since they can provide the molecular parameters which are independent of intermolecular interactions. It is convenient to measure the NMR parameter as a function of density and the extrapolation to zero density gives the exact measurement for an isolated molecule [4,5]. The medium effects can be studied quantitatively when the NMR parameter for an isolated molecule is used as the reference standard. The gas-phase results are also attractive for ab initio studies since the calculations can actually model shielding tensors for small molecules with high accuracy [6,7]. Using new NMR techniques we could observe extremely weak ^{17}O and ^{33}S NMR signals from the gas phase, cf. the ^{17}O NMR spectrum for gaseous acetone [8]. It has also enabled us to monitor the ^{17}O and ^{33}S NMR spectra for a set of small molecules (CO, CO_2, N_2O, OCS, SF_6 and others) in the gas phase. For the first time we could measure their chemical shifts and some spin-spin coupling constants as the function of density. Our new results include the ^{17}O and ^{33}S NMR parameters for isolated molecules, their temperature dependence and the second virial coefficients which are responsible for intermolecular interactions. The latter data reveal that the intermolecular contributions to oxygen shielding are more negative than similar effects observed for lighter nuclei like ^{13}C or ^{15}N. In contrast the ^{33}S shielding in sulfur hexafluoride is only modestly influenced by intermolecular interactions what is probably due to the octahedral symmetry of a SF_6 molecule.

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OC4

HYDROGEN-BONDS, WATER MOLECULES AND HYDRATION MECHANISMS IN MACROMOLECULES AS STUDIED BY INFRARED SPECTROMETRY

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This presentation is aimed at illustrating the power of infrared (IR) spectrometry to study the structure and the reactivity of an important and ubiquitous molecule, which incidentally plays a fundamental role in biomechanisms but is still poorly known and consequently often ignored: **H_2O**. Because of its unique ability to establish or accept a great number of hydrogen-bonds, H_2O displays exceptional properties: an assembly of such molecules, such as found in liquid water, exhibits exceptional physical and chemical properties, the origin of which is still not well understood at molecular level. In macromolecular systems it is always present and more or less modifies the properties of these systems, up to the point where it may be at the origin of their reactivity, as in biosystems.

This molecule is not easy to look at and this explains why it is often neglected. Thus powerful methods to study macromolecules, such as scattering of X-rays or neutrons, encounter difficulties to observe such small and versatile molecules, which are often at the origin of spatial disorder. NMR is not especially sensitive to them. The astonishing point is that IR spectrometry, a highly precise method to study hydrogen-bonds, has scarcely been used to observe H_2O. This is due to problems of saturation of bands, which find their origins in the great sensitivity of IR to hydrogen bonds and paradoxically reach such a point that H_2O is often considered a poison in IR spectroscopy.

If one is sufficiently careful to avoid such drawbacks, IR spectrometry indeed reveals a powerful method to study the hydration process(es) of many macromolecular systems. We shall illustrate this point, describing the procedures used to study the various steps of hydration and displaying examples of hydration spectra of macromolecules ranging from synthetic polymers, such as epoxy-resins, to proteins, including such biopolymers as polysaccharides. These examples will also illustrate how these hydration spectra allow to determine the hydrogen bond configurations that H_2O molecules choose to adopt among the numerous possible ones, and also how they give information on related mechanisms such as progressive ionization of COOH carboxylic groups. Indications will also be given as to how IR spectrometry may soon look invaluable to study the crucial role of H_2O molecules in such a process which has up to now been scarcely considered, but more and more appears as a fundamental mechanism in aqueous media, especially biological media: transfers of protons through hydrogen-bonds.

VIBRATIONAL COOLING OF POLYATOMICS IN EXCITED ELECTRONIC STATES - THEORY AND EXPERIMENT.

OC5

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The weakening of vibrational frequencies in electronically excited states of polyatomics can be utilised to singinifcantly cool the vibrational population in the exctied state. This cooling can lead for example to significant slowing down of unimolecular isomerization rates. The dependence of the cooling on excitation frequency, buffer gas pressure as well as the resulting time and frequency resolved fluorescence decay curves will be discussed. New experimental measurements on the trans-Stilbene system, confirming the predicted cooling will be presented.

OC6

CONFINEMENT DYNAMICS OF MOLECULAR LIQUIDS PROBED BY QUASI-ELASTIC NEUTRON SCATTERING

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In this work we report the Incoherent Quasi Elastic Neutron Scattering (IQENS) features of an H-bonded liquid and a molecular one, namely Ethylene Glycol [EG]: HO-CH_2-CH_2-OH, and Ethylene Glycol Dimethyl Ether [EGdE]: CH_3O-CH_2-CH_2-OCH_3, respectively. We analysed the samples in bulk and confined in silica gel matrix (Gelsil glass, 26Å diameter pores), at different temperatures.

It is well known that the static and dynamic properties of bulk liquids may undergo a dramatic modification, induced by confinement, due to interation forces (Van der Waals, Hydrogen Bond) with the substrate molecules and to geometrical restriction (excluded volume effects) when the system is forced to diffuse into small pores whose dimension is slightly bigger than the size of the fluid molecules. Generally speaking, the fluid in the pores has one phase related to the surface-fluid interface whose properties are triggered mainly by surface forces. These latter can be attractive or repulsive depending on the polarity, adsorption energies and surface coverage (hydrophilic or hydrophobic groups existence). The other phase can be related to the inner pore volume and may be driven by intermolecular interactions, shape of molecules collective hydrodynamic effects and so on. In order to study dynamic properties of liquids that diffuse, reorient and vibrate in a confined geometry two relevant effects must be considered: *physical traps* which are related to the topological environments and *chemical traps* that take into account the degree of adsorption of the active inner surface sites.

The experiment was performed by the IN6 t.o.f. spectrometer on the above mentioned samples at the following temperatures: T=-35°C, -12°C, 20°C, 40°C. The data analysis has shown a clear different diffusive dynamics, revealed by the observed faster behaviour in the case of EGdE that doesn't suffer the absorption effects due to its molecular character.

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CHEMICALLY MODIFIED FIBRE-OPTIC SERS SENSOR FOR THE DETECTION OF ENVIRONMENTAL CONTAMINANTS

OC7

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Surface-enhanced Raman scattering (SERS) is a fast and sensitive technique to detect submonomolecular layers of molecules adsorbed at rough metal surfaces. Fibre-optic sensors based on SERS can serve for sensitive, remote chemical analyses with alignment-free exchange of samples and without freely propagating laser light. In the so-called optrode design, a single fibre carries both, excitation radiation and Raman-scattered light, and the fibre tip is modified into a SERS-active surface. A great variety of techniques can produce SERS-active substrates, and some of them have been shown to be applicable at fibre tips [1]. In the present investigation, fibre sensors are prepared by vacuum deposition of metal films on tips dip-coated with alumina nanoparticles. The SERS-active metal surfaces exhibit rather unspecific adsorption properties and are chemically reactive. Poisoning of the surfaces and adsorption of unwanted substances can be avoided by organic modification of the metal surfaces with selectively adsorbing receptor molecules. These receptors can furthermore enhance the adsorption of analyte molecules, and thus lower the limits of detection. For instance, the modification of SERS-substrates with cage- or cone-like molecules as calixarenes [2] or cyclodextrins [3] yield surfaces capable of adsorbing lowly concentrated aromatics from the gas or liquid phase.

The present investigation demonstrates the chemical modification of the tips of fibre-optic SERS sensors, and the application of the modified sensors in the detection of environmental contaminants. Calix[n]arene molecules with n = 4, 6 and 8 have been thio-derivatised and then chemically bonded to the SERS-active surfaces at the fibre tips. These calix[n]arene-coated sensors have been applied in the detection of different organics in water. As expected, receptors with smaller cages have preferentially adsorbed smaller guest molecules and vice versa. Detailed investigations have been done on the detection of traces of explosives like picrid acid and of aromatics in water.

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OC8

SPECTROSCOPY IN ENVIRONMENTAL PROTECTION, COMPARATIVE IR AND ^{13}C NMR STUDY OF CHLOROFLUROCARBONS

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Chlorofluorocarbons (for example CCl_2F_2) emitted into the atmosphere are responsible for ozone depletion in the stratosphere. Consequently, due to global environmental concerns, the production and use of CFCs are currently being phased out under international agreements, Montreal Protocoll [1] and its subsequent revisions.

Their potential substituents, the hydrochlorofluorocarbons (like $CHClF_2$) are permitted tc use only temporarily. Nowadays, besides the replacement, there are also other problems such as storage, treatment and safe destruction of CFCs produced until 1996 and that have been phased out now.

IR and ^{13}C NMR studies of CCl_2F_2 and $CHClF_2$ decomposition over solid catalysts were carried out monitoring the gaseous, liquid and adsorbed phases. IR spectra of the reactants adsorbed on self-supported wafers pressed from zeolites and their gaseous products were taken with a Matson Genesis FTIR spectrometer. ^{13}C NMR spectroscopic investigations of the starting materials in liquid phase and the products of surface reactions over different zeolites measured in sealed tubes were performed using a Bruker MSL 400 spectrometer.

Results obtained by IR spectroscopy revealed that the decomposition of CCl_2F_2 and $CHClF_2$ generates different surface species, suggesting different reaction mechanisms. For CCl_2F_2 the formation of $COCl_2$ as surface intermediate is proved by the doublet appearing at 1800 and 1710 cm^{-1} caused by Fermi resonance [2].

The variation of chemical shifts together with the changes in carbon-fluorine coupling constants showed that the $CHClF_2$ molecule interacts quite differently in the liquid and adsorbed states on zeolites NaY and HZSM-5.

The IR and ^{13}C NMR spectroscopic results are in good agreement and proved that intermediates of the surface reactions of CCl_2F_2 are CCl_4, $COCl_2$, while the gaseous end-product is CO_2. For $CHClF_2$ the intermediate is $CHCl_3$, the final gaseous product is CO. The fluorine contained of both reactants appears in the solid phase as AlF_3 [3].

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RECENT DEVELOPMENTS IN MID-IR FIBER OPTIC SPECTROSCOPY FOR ANALYTICAL APPLICATIONS

OC9

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Infrared spectroscopy plays an important role in analytical chemistry for component identification and quantification. For the analysis of solid and liquid samples, the attenuated total reflection (ATR) technique is well suited. A comparison of conventional ATR accessories with silver halide fiber probes in the past has shown their potential (1). Flexible fiber probes based on silver halide materials have several advantages, since they allow remote sensing and a fast and easy sample measurement in the wavelength region from 3 µm to 20 µm (2). This region is otherwise only accessible by rigid light guide systems based on mirror optics. Most of our previous applications were within clinical chemistry (3). The new sensors reported here have an improved long-term stability and a spectral signal-to-noise ratio can be achieved to reliably reach subpromille concentrations of glucose in biotic fluids for example. Several probe geometries based on different fiber cross-sections are presented, and their individual advantages are reported. For ultimate sensitivity with a Fourier-Transform spectrometer, a set-up with a single fiber coupled directly to a liquid nitrogen cooled MCT-detector element is favoured. For routine analysis exchangeable sensor probes have been used, e.g., for authentication and purity check of virgin olive oil samples. Different protective fiber coatings were applied, some rendered the intensification of absorption signals by about a factor of 10 compared to uncoated fibers by interference amplification. Examples are presented for aqueous solutions of organic solvents, and current limitations for IR-spectroscopic trace analysis are discussed.

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ABSTRACTS
ORAL CONTRIBUTIONS - **INTAS**

FLUORESCENCE PROPERTIES OF THE DOXORUBICIN IN SOLUTIONS AND ADSORBED ONTO THIN SILVER FILMS

OI1

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This work describes fluorescence of a potent antitumour agent, related to antracycline antibiotic, doxorubicin (DOX) in solutions and adsorbed onto surface of annealed and chemically modified vacuum deposited thin silver films (TSFs). In all cases a spectrum of fluorescence has a well expressed vibration structure. A position of vibration bands in fluorescence spectrum of DOX (557, 589 and 639 nm) practically does not depend on polarity of a solvent and surface properties, however the relative intensities of vibronic bands vary. In water solutions the measured value of a fluorescence quantum yield of DOX has lowest values (4.7% at pH=5.1), depending on pH of solution. When pH of solution changes from 3.1 to 11.7 the fluorescence quantum yield decreases approximately in 3.5 times and the position of vibration bands in spectra does not change. In the aprotic organic solvents the intensity of DOX fluorescence is higher (approximately in 3 times) than in water solutions. It allows to assume, that the water is effective quencher of fluorescence of DOX. More probably a mechanism of this is the charge transfer.

When DOX is adsorbed onto a surface of the TSFs, the enhancement of fluorescence is observed. This phenomenon depends on the optical properties of TSF. Changing method of TSFs modification allows to register the surface-enhanced Raman scattering spectra (SERS) or spectra of surface-enhanced fluorescence (SEF) of DOX, adsorbed onto surface of the modified substrate. With use of excitation wavelenght near the maximum of TSFs plasmon resonance band the SEF is mainly observed. When the maximum of optical density of TSF is blue-shifted from resonance conditions, the SERS of adsorbed DOX is also observed. The greatest enhancement of fluorescence is registered when DOX is adsorbed onto chemically modified annealing TSFs. The intensity of fluorescence per one molecule adsorbed onto TSF, modified by NaCl is higher in 7.5 times, than the intensity of fluorescence per one molecule, adsorbed onto quartz plate.

The obtained results show a possibility of selective registration of one or another component of the secondary emission (SERS or SEF) of DOX, adsorbed onto TSF by tuning of substrate optical properties. The mechanisms of surface enhancement of secondary emission of DOX are discussed. The formation of secondary emission spectra of DOX, adsorbed onto chemically modified TSFs depends, probably, on interactions of analyte molecules with the surface plasmons in conditions of excitation close to resonance.

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THE SERS STUDY OF THE DOXORUBICIN ADSORBED ONTO CHEMICALLY MODIFIED THIN SILVER FILMS

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This work presents the newly created substrates adapted for its applications in the surface enhanced Raman spectroscopy (SERS) of antitumour drugs. Careful selections of optimal protocol of annealing and of the following chemical modifications of annealed surfaces of vacuum deposited thin silver films (TSFs) allow obtaining substrates with various physical and chemical properties. This leads to variation of microenvironment properties for the adsorbed analyte molecules. The SERS spectra of doxorubicin (DOX) (Fig. 1.) obtained with use of such TSFs are discussed in this report.

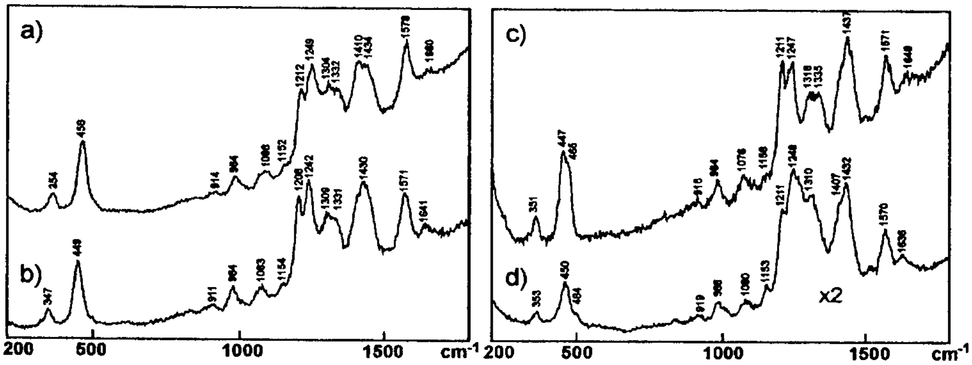

Fig.1. The SERS spectra of DOX adsorbed onto the annealed TSFs without chemical treatment (a,d), TSF after HCl (b), and acetonitrile (c) treatment without poly-L-lysine coating on the DOX monolayer (a-c), and with poly-L-lysine coating (d) (λ_{ex}= 488 nm, P=5 mW on a sample).

In the SERS spectrum of DOX adsorbed onto chemically modified by HCl and acetonitrile TSFs the strong band at 458 cm^{-1} (δ(C=O)) and very weak band at 1660 cm^{-1} (ν(C=O)) are shifted to lower frequencies in comparison with their positions in the SERS spectrum DOX adsorbed onto TSF (ca. 19 cm^{-1} and 12 cm^{-1}, correspondingly). The intensity of strong band at 1212 cm^{-1} (ν(C-O)+δ(C-O-H)+δ(C-H)) and bands of medium intensity at 1304/1332 cm^{-1} (ν(C-O)+δ(O-H)), 1410/1434 cm^{-1} (ring stretch + ν(C-O)) are very sensitive to the surface properties of TSFs.

The coating of the adsorbed DOX by poly-L-lysine leads to the quenching of the fluorescence background. Under such conditions the relative intensities of bands at 450 cm^{-1} (δ(C=O)) and 1570 cm^{-1} (ν(C=C)+ν(C-O)) are weak and the band at 1660 cm^{-1} (ν(C=O)) is shifted to lower frequency (ca. 24 cm^{-1}) in comparison with its position in the DOX SERS spectrum (Fig. 1, a).

Influence of molecular processes near the substrate surface on the DOX SERS spectra in various conditions are discussed.

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SERS SPECTROSCOPY ANALYSIS OF AZA-15-CROWN-5-ETHER CONTAINING SPIRONAPHTHOXAZINE AND ITS COMPLEXES WITH METAL CATIONS

O13

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Aza-15-crown-5-ether derivative of spironaphthoxazine (crown-SNO) was synthesised in order to combine the remarkable photochromic properties of SNO with the ability of a crown ether to form a complex with a metal ion. Here we present the first results on the development of a surface-enhance Raman scattering (SERS) approach to the study of crown-SNO and its complexes with metal cations.

An electrochemically roughened silver electrode was used as a SERS-active substrate that enabled one to measure SERS spectra of an analyte in any organic solvent and to vary widely an ion composition of a solution. Crown-SNO exists in acetonitrile mainly in a colorless spiro form, while UV irradiation reversibly converts it into a colored merocyanine form. In spite of predominance of a spiro form, it was found that a merocyanine form of crown-SNO can be selectively traced by means of SERS spectroscopy with 514.5 or 647.1 nm excitation due to the resonance enhancement of SERS signal of the colored species. Fluorescence, that prevents from resonance Raman spectrum recording of SNO derivatives, is quenched for the molecules adsorbed on the SERS-active surface. Therefore, SERS technique can serve as an alternative to the time-resolved Raman spectroscopy in the investigation of the ground state equilibrium structure of a merocyanine form of SNO derivatives.

The SERS spectrum of crown-SNO was compared to the spectra of morpholine derivative of SNO and its molecular fragments: di- and tri- substituted naphthalenes, crown containing naphthalene, and indoline moiety, that enabled the adsorption geometry of crown-SNO at the SERS active surface to be revealed. The results of the investigation show that basing on SERS spectra a state of merocyanine oxygen can be identified in different solvents (free, hydrogen bound to solvent molecules or protonated).

The formation of complexes with metal cations was found to be accompanied by the pronounced changes in SERS spectra. The interactions affect weakly the positions of SERS bands, but induce notable changes in their relative intensities. The ratios (R) of 926 and 474 cm^{-1} band intensities to 556 cm^{-1} band intensity were found to be characteristic for such interactions. R(926/556) and R(474/556) are equal to 0.9 and 1.6 in the spectrum of free crown-SNO and change to 1.9 and 0.5, respectively, upon metal cation binding. These ratios were used to characterise peculiarities of crown-SNO/cation complex formation for Ba^{2+}, Mg^{2+} and Eu^{3+} cations.

Acknowledgment: The work was supported by the INTAS grant No 97-31193.

O14

RAMAN SCATTERING SPECTROSCOPY STUDY OF THE DNA STRUCTURAL ALTERATIONS INDUCED BY THE ANTITUMOR MINOR GROOVE BINDERS BIS-NETROPSINS AND POLYAMINES.

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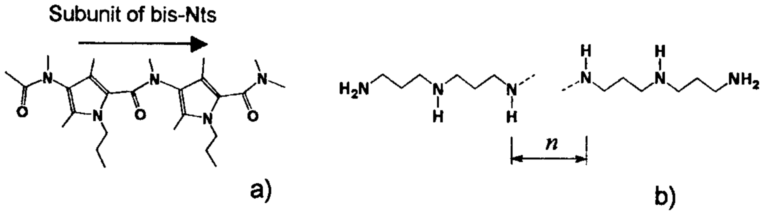
Structural alterations of the DNA upon the interaction with the new antitumor minor groove binders - bis-netropsins (bis-Nts) and polyamines (PAs) were studied by Raman scattering spectroscopy technique.



a) b)

Fig. 1. Chemical structures of bis-Nts' subunit (a) and of synthetic hexamines (b).

Effect of bis-netropsins.

Three types of bis-Nts differed by orientations of their subunits (Fig. 1a) and three type of oligonucleotides (specific and non-specific binding) were studied. The bis-Nts specific as well as non-specific binding does not change the backbone parameters of DNA, which were found to be in the B-conformation. Nevertheless, the small modifications of oligonucleotides secondary structure, perturbations of stacking interactions of adenine, local changes of topology in the vicinity of thymines and guanines are observed. The last is the most important because it demonstrates that drug-induced DNA structural perturbations involve not only the sites of direct bis-Nts binding, but also the spatially distinct sites.

Effect of polyamines.

New synthetic hexamines with the $(CH_2)_n$ central chains (n = 10, 12, 14, and 16 (Fig.1b)) were used in the structural studies of polyamines/DNA interactions. Noticeable changes in Raman spectra of PA/DNA complexes in comparison with pure oligonucleotide were observed in spectral ranges 750-840 and 1478-1490 cm^{-1}. Correlation between relative intensities of some spectral lines and the length of the PAs central chain were found. The greatest spectral and consequently structural changes for hexamine with the shortest central methylene chain were observed.

We hope that effects of DNA structural modification being found by Raman scattering spectroscopy may explain the inhibition features of some antitumor minor groove binders.

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FOURIER TRANSFORM RAMAN SPECTROSCOPIC CHARACTERIZATION OF CELL SURFACE CONSTITUENTS OF THE SOIL BACTERIUM *AZOSPIRILLUM BRASILENSE*

O15

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Many physicochemical aspects of plant-microbe interactions still remain largely unknown, and the application of molecular spectroscopic techniques to both bacterial and plant metabolites which are directly involved in contact interactions can provide necessary structural information.

In this work, a set of isolated preparations of lipopolysaccharides (LPS), LPS-protein complexes and polysaccharide-lipid complexes, which are typical for the plant growth-promoting nitrogen-fixing rhizobacterium *Azospirillum brasilense*, were studied for different strains of this bacterium (in particular, strains Sp7 and Sp245) which are known to occupy different ecological niches with regard to their interaction with roots of host crop plants and induce different responses of the latter. As LPS- and protein-containing cell surface constituents are involved in contact interactions of azospirillum with host plant roots, their physicochemical properties and structural features may provide an insight into the molecular mechanisms of plant-bacterium interactions. The FT-Raman technique, which is most informative for less polar functional groups like lipid moieties (fatty acid residues), has shown certain differences in the lipid components of the LPS-containing samples studied. In concert with FTIR data which are more informative for polar groups (polysaccharide and protein moieties) [1], the information obtained allows some structural and compositional properties of the bacterial cell surface biopolymers to be characterized.

Dried intact bacterial cells of different strains of *A. brasilense* were also studied using FT-Raman spectroscopy. While FTIR data [1,2] gave an overall "fingerprint" picture of the cell composition, FT-Raman spectra featured, among others, the most pronounced lipid bands related to LPS and phospholipids of the cell wall which are less informative in IR, thus providing complementary information.

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O16

ACETONE-BUTANOL (ABE) FERMENTATION MONITORING BY INFRARED SPECTROSCOPY OF BACTERIAL CELLS

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Analysis methods using Infrared spectroscopy of microbial cells have found their place for microbial biomass studies, bioprocess monitoring and fermentation process optimisation (1, 2, 3).

Microbial biomass of strain *Clostridium acetobutylicum* ATCC 824 was grown under three different fermentation conditions: 1) strictly anaerobic conditions with vegetative inoculum; 2) semi-anaerobic conditions with vegetative inoculum; 3) strictly anaerobic conditions with spore inoculum. Vegetative inoculum of *Clostridia acetobutylicum* under semi-anaerobic growth conditions and spore inoculum under strictly anaerobic conditions produced solvents at high level. Vegetative inoculum fermentation under strictly anaerobic growth conditions showed an "acid crash", i.e. produced mainly acids and did not switch to predominant solvent production.

On the basis of the Beer Law and a system of Vierordt equations for the principal components - carbohydrates, nucleic acids, proteins and lipids, quantitative analysis of microbial biomass was carried out (3,4).

The obtained data for studied ABE fermentation versions confirmed that butanol production increase takes place at definite biomass physiological state. Correlation is observed between the principal cell component content and the onset of butanol production. The content of nucleic acids decreases with process time, and the lipid content increases, corresponding to ceasing growth and the formation of toxic fermentation products. It can be concluded that analysis of biomass components is a promising tool for the characterisation of this and other complex bioprocesses.

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ULTRAFAST PHOTOPHYSICS OF NON-RIGID PORPHYRIN SYSTEMS

O17

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It is commonly accepted for porphyrins, and for tetrapyrrole molecules in general, that any remarkable intramolecular quenching of their excited states is possible only as a result of a presence of special "quenching units" in the tetrapyrrole structure. Heavy atoms, transition metals or electron donor/electron acceptor groups may play a role of such "quenching units". It has been recently found, however, that there are examples of porphyrin structures in which none of such special "quenching elements" is available but, nevertheless, their excited $^1(\pi,\pi^*)$ states are strongly (up to ~1000 times) quenched as compared to the corresponding excited states of normal porphyrins. Two such types of porphyrin systems, which may be called "porphyrins with non-rigid π-conjugated macrocycle" (or "non-rigid porphyrins"), have been revealed: (1) ethylene-bridged porphyrin dimers [1], and (2) porphyrins having nonplanar macrocycle [2,3].

With the aim to elucidate the mechanisms responsible for such ultrafast photophysics, both these types of unusual porphyrin systems were studied in this work by the methods of picosecond time-resolved fluorescence and femtosecond transient absorption: (1) the ethylene-bridged octaethylporphyrin dimers H_2OEP- H_2OEP, H_2OEP-ZnOEP and ZnOEP-ZnOEP in both *cis*- and *trans*-conformations, and (2) nonplanar porphyrins including a series of dodecasubstituted porphyrins with increasing degree of nonplanarity (from tetraethyl-TPP to octaethyl-TPP) as well as a series of nonplanar diacids of normal porphyrins (such as H_2OEP and H_2TPP).

We have shown that, for both these types of porphyrin systems, structural distortions in the excited state are responsible for the found very effective internal conversion S_1~~>S_0. A qualitative model is proposed which explains numerous unusual photophysical properties of these non-rigid porphyrin systems as a result of an existence of decay funnels on the potential energy surface of the excited $^1(\pi,\pi^*)$ state. The decay funnels are suggested to be conical intersections of the ground and excited state surfaces in the case of the porphyrin dimers. Reaction coordinates (i.e. the types of structural distortions) leading to the decay funnels will be discussed.

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O18

STRUCTURE AND HYDRATION OF POLYCYTIDYLIC ACID FROM THE DATA OF INFRARED SPECTROSCOPY, E H F DIELECTROMETRY AND COMPUTER MODELING

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The polyribocytidylic acid [poly(rC)] is known to form different structures in aqueous solutions in the dependence on pH, temperature and ion content. At room temperature and neutral pH poly(rC) is an ordered single-strand helix. In the range $3.7 < \mathrm{pH} < 5.5$ it forms a helical double-strand complex in which a proton is added to the ring nitrogen for each pair of bases. Below pH 3.5 a dissociation into two disordered chains with protonated cytosines occurs. The aim of present work is to elucidate the role of water environment in the formation of these different structures of poly(rC). To solve this problem we studied the hydration of poly(rC)-Ka$^+$ in the wet films with various water content by methods of infrared (IR) spectroscopy, piezogravimetry and in the solutions by EHF (extremely high frequencies) dielectrometry.

The IR spectra of poly(rC) with different values of n (n is the number of water molecules per nucleotides) were recorded with spectrometer UR-20 in the regions of absorption of cytozine (1500 -1750 cm^{-1}), sugar phosphate backbone (900-1350 cm^{-1}) and sorbed water (2900-3800 cm^{-1}). A resonant quartz crystall technique has been used to obtain water sorption isotherms (hydration isotherms) for poly(rC) at different pH and temperature. The dielectric measurements of poly(rC) solutions (1%) at different pH (8, 4.5, 3.3) and T=23^{0}C were carried out by differential microwave dielectric method developed by us. From these measurements the decrement of the complex dielectric permittivity and degree of polynucleotide hydration have been determined. From the analysis of hydration isotherms, spectral isotherms and spectral parameters (frequencies and intensities of the main bands) in the dependence on n ($0<n<2\text{-}3$) the same hydration sites of poly(rC) at pH 8 and 4.6 were determined (N1,N3, C2O, N4H2, (base), 04 and C2`OH (ribose), PO$_2^-$ (phosphate)). It was found that the transition of polynucleotide from the unordered state to the double stranded complex poly(rC) at pH 4.6 occurs in the interval $2<n<8$. Final stabilization of the complex takes place with increase in the water content to n=9. This value fully agrees with EHF findings for poly(rC) solutions. Thus, this amount may be considered to be necessary for stabilization of double-helix poly(rC) both in solution and in films. These experimental results have been confirmed by the Monte Carlo simulations of interaction poly(rC) components (cytosine, cytidinemonophosphate, their protonated derivatives and tetranucleotides (rC) in single and double-stranded forms) with water molecules. The bridges of water molecules connecting pair of bases along the chain and bases with sugar-phosphate backbone of their chains in single-strand and also base pairs in opposite chains of double-strand poly(rC) are found out. In conclusion a model of hydration of double-strand complex poly(rC) based on our results and known X-ray parameters has been proposed. The obtain results suggest that stabilization of this complex occurs due to intra- and interchain water bridges along with hydrogen bonds between cytosines in pairs.

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TIME CORRELATION FUNCTIONS FROM BAND-SHAPE FITS WITHOUT FOURIER TRANSFORM

O19

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A novel fitting method is described enabling one to model real line profiles intermediate between Lorentzian and Gaussian by an analytical function which has an analytical counterpart in time domain [1]. Specifically, the time correlation function is written in the form

$$G_v(t) = \exp\{-[(t^2 + \tau_1^2)^{1/2} - \tau_1]/\tau_2\},$$

and its Fourier transform reads

$$I(\nu) = 2nc\exp(\tau_1/\tau_2)(\tau_1^2/\tau_2)K_1(x)/x,$$

$$x = \tau_1[4\pi^2c^2(\nu-\nu_0)^2 + 1/\tau_2^2]^{1/2},$$

where $K_1(x)$ is the modified Bessel function of the second kind, ν_0 is the peak wavenumber, n=2 if ν_0=0 and n=1 if $\nu_0 \neq 0$.

The applications of this method comprise (i) finding time correlation functions and correlation times by fits in frequency domain without Fourier transforms, and (ii) decomposition of overlap lines obtaining dynamic parameters at the same time.

The working ability of the method is demonstrated using the isotopic structure of the ν_1 line in the isotropic Raman spectrum of liquid carbon tetrachloride. The time-correlation functions of vibrational dephasing have first been found for each isotopic species present in the liquid in the natural abundance. The isotopic dependence of the characteristic times of vibrational dephasing and vibrational frequency modulation has been analysed. The dephasing times decrease with decreasing the line frequency. This dependence entirely outweighs the opposite relationship between the dephasing times and masses. The frequency modulation times show the same trend, which contradicts to the simple collision model.

Numerous other examples will also be shown, including some liquids [2] and glasses [3], and, especially, an impressive "global fit" of the Raman spectra of liquid formamide performed in the whole spectral region (10-4000 cm^{-1}).

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ABSTRACTS
POSTERS - SESSION (1)

Spectroscopy in Astrophysics

VISIBLE SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS IONIC DERIVATIVES : APPLICATION TO ASTROPHYSICS

P1.1

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The understanding of physical and chemical processes in the interstellar medium is currently an important challenge for our Universe knowledge since these processes are involved in the control of stars and planets formation.

Polycyclic Aromatic Hydrocarbons (PAHs) are now recognized as an important constituent of the interstellar medium gaseous phase, mainly through observations of their IR emission bands. This family of molecules and in particular their ionic and radical derivatives seems to be one of the most promising candidates for identification of Diffuse Interstellar Bands (DIBs). These absorption bands, observed - throughout the visible and near infrared spectral range - over spectra of stars masked by gas cloud, were first discovered in 1922. Their properties indicate that DIBs could originate from gaseous phase carbonaceous molecules. The possible identification of PAHs as molecules responsible for these bands must be done through direct comparison with PAHs spectra recorded in conditions as close as possible to those of the interstellar medium.

These low temperature and collision-free conditions can be recreated in the laboratory with supersonic beams. The spectroscopic methods used to probe the beam must be very sensitive since ions cannot be produced in large quantities. In our laboratory, PAH ions are formed by resonant two-photon ionization with two tunable lasers, and the absorption of a third laser beam is detected by a time-of-flight mass spectrometer. This mass spectroscopic detection supposes that the photon absorption induces a change in the molecule charge or mass, which cannot be produced by a visible photon. This problem was solved by ionizing a van der Waals complex formed by the association of the molecule under study and an argon atom, the third photon absorption causing argon departure. The PAH cation visible spectrum is recorded while monitoring the fragmentation ratio as a function of the energy of this photon. These absorption signatures give acces to the searched spectrum, since rare gas atom adsorption is a very small perturbation for the electronic transitions. With this technique, several spectra of PAH cations could be obtained, spectra which were compared with DIBs spectra seen in the litterature.

Moreover, an observation campaign with the Télescope Bernard Lyot at the Pic du Midi was carried out and should allow us to perform a systematic search for correspondence between the bands observed in experimental spectra and in astronomical spectra.

P1.2

ATMOSPHERE SPECTROSCOPY: NONLINEAR OPTICAL EFFECTS

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In process of the IR laser radiation (LR) resonance absorption in atmosphere it occurs the redestribution of molecules on energy levels of internal freedom degrees.Creation of the excited nitrogen molecules due the resonance excitation transmission from carbon dioxide molecules leads to the medium polarizability changing.As result it could be substantionally changed the IR LR propogation conditions. Here we consider the role of resonance spectroscopic effects in the forming of the nonlinear atmosphere gases behaviour for propogation of the powerful LR pulses under different conditions and atmosphere models.As a basic model for the absorbed energy relaxation description it's used 3-mode kinetic processes model. It's numerically shown the change in the time dependence of the resonance radiation absorption coefficient for carbon dioxide under different conditions. Stimulated light scattering in atmospheric gases are also considered. On the basis of the operator perturbation theory form and QED moments technique [1] it's developed the effective approach for description of the LR atmosphere multi-photon absorption and Stark dynamic shift (these effects can be used as the physical basis for new distance methods of environment laser diagnostics). We have calculated shift &width for 3-photon resonance, 4-photon ionization profile of atomic hydrogen (transition 1s-2p; wavelength 365nm; UV multimode Gauss pulse: band width 0.25 см^{-1}). It's received a good agreement with the experiment data of Kelleher etal & Zoller stochastic calculation. We also examined effect of 2-photon LR adsorption on vibration-rotational molecular transitions: CO_2 LR (intensity: 10^7 W/cm^2) in the water steam 010 band and received for 2-photon adsorption probability~$(2\text{-}3)10^9$ c^{-1},that is in agreement with result of Letokhov &cow.[2]: (1-1,5) $10^9 c^{-1}$; it's on several orders less than the value of one-photon process probability .

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LINE SHAPE ANALYSIS IN THE MICROWAVE AND INFRARED RANGES

P1.3

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The detection of minor components in terrestrial or planetary atmospheres by spectroscopic techniques implies not only the knowledge of the line frequency but also the knowledge of the line shape, in order to retrieve their concentration. The foreign gas collisional broadening parameters are usually determined from millimeterwave or infrared spectra, by using a traditional Voigt profile. In some cases some deviations from this profile are observed experimentally and other profiles can be tested, including effects such as speed dependant relaxation or molecular diffusion [1].

The reported results are connected with space missions for the observation of earth atmosphere (project linked to the satellite Odin, planned to be launched this year) or the atmosphere of Titan (a satellite of Saturn which will be reached by the Cassini mission in 2004). These results concern the oxydes NO and N_2O on the one hand and the nitriles HCN and CH_3CN on the other hand, the collision partners being the major species in the corresponding atmospheres. The measurements have been made at different temperatures in the range 240-350K. This allows the retrieval of the temperature dependence of the broadening parameters.

For methyl cyanide CH_3CN, N_2, H_2 and He has been used as perturbers. The K dependence of the line profile will be discussed. Experimental results dealing with the J=12-11 rotational transition for K values from 0 to 11 will be compared to calculated values using the ATC formalism.

For NO and N_2O, submillimeter transitions were observed and the collisional broadening by O_2 and N_2 thoroughly analyzed, using different theoretical profiles (Galatry profile, Speed Dependent Voigt profile...). In the case of NO the problem is more complex due to the hyperfine components which are partially resolved. The parameters retrieved with different profiles will be compared.

Finally infrared data will be presented , dealing with the nu2 band of HCN perturbed by rare gases, N_2 and polar molecules. The results obtained with various profiles at room temperature will also be discussed, and compared with previous results obtained in the millimeter range.

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Gas Phase / High Resolution Spectroscopy
Microwave Spectroscopy

SIMULATION OF INTERNAL METHYL ROTATION IN CH STRETCHING OVERTONE SPECTRA OF TOLUENE

P2.1

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The vapor phase overtone spectra of toluene-d_0, α-d_1 and α-d_2 in the CH stretching region have been recorded at room temperature. The vibrational overtone spectra were recorded with conventional near-infrared, and with intracavity titanium:sapphire and dye laser photoacoustic spectroscopy. The aryl region of the overtone spectra is virtually identical in all three molecules and can be understood on the basis of two non-equivalent aryl local modes. The methyl region differs significantly in these three molecules, with respect to relative intensity, line width and structure.

We simulate the spectra, by describing the CH stretching modes within the harmonically coupled anharmonic oscillator local mode model and the methyl torsional mode by a rigid rotor model. The parameters used for the simulation, such as the dipole moment function, frequency, and anharmonicity, are obtained from *ab initio* calculations. We compare our simulations with a simpler model, which introduces an adiabatic approximation between the methyl rotation and the CH stretching. Good agreement is found between the observed and simulated spectra. We found that the time scale for the CH stretching coupling is slower than the time scale for the internal rotation.

P2.2

THE PEPTIDIC GROUP ACTS SIMULTANEOUSLY AS PROTON DONOR AND PROTON ACCEPTOR WITH RESPECT TO AN ADJACENT HYDROXYL GROUP: FREE JET SPECTRUM OF LACTAMIDE.

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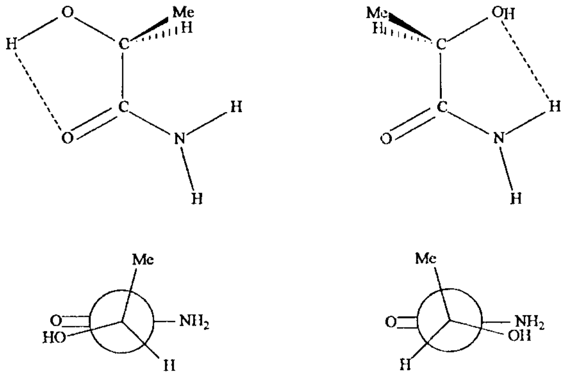
The rotational spectra of two nearly isoenergetic conformers of lactamide (a chiral molecule) have been assigned with free jet millimeter wave absorption spectroscopy. In the experiments the sample, heated to 130 °C, was seeded in Ar at 30 kPa and expanded to about 0.2 Pa through a nozzle with a 0.3 mm diameter.

The study of several isotopic species showed that both conformers are stabilised by an intramolecular hydrogen bond formed between the peptidic group and the adjacent hydroxyl group. In one case (conformer I) the hydroxyl group acts as a proton donor, while the reverse is true for conformer II, (see Fig. 1).



CONFORMER I

CONFORMER II

Fig. 1 – Observed conformers of lactamide

Ab initio calculations at various levels of theory (HF 6-311G**, B3LYP 6-311G**, B3LYP 6-311++G**...) confirmed the two observed conformers to be stable points with about the same energy. None of the calculations was suitable to reproduce the geometry of conformer II.

MICROWAVE FOURIER TRANSFORM SPECTROSCOPY: APPLICATION TO MOLECULES AND VAN DER WAALS COMPLEXES

P2.3

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A microwave Fourier transform spectrometer coupled to a supersonic expansion is a powerful tool for the study of weakly bound molecular complexes but also normal molecules in the gas phase by probing their low-lying rotational states, the rotational temperature in the jet being only several kelvins. Some studies using our recently built MWFT spectrometer, operating in the frequency range 6-20 GHz, will be presented.

Vinylstibine and ethynylstibine are two molecules (more or less stable : 2-3 days for vinylstibine, one hour for ethynylstibine)) newly synthethised by the group of J. C. Guillemin in Rennes (France). The analysis of the spectra of the mother species, coupled to the study of some isotopic species (^{13}C, ^{121} Sb, ^{123}Sb) produces some structural information on these molecules. The C-Sb bond length has particularly been the subject of our investigations. The quadrupole coupling constants of ^{121}Sb and ^{123}Sb have also been determined.

The van der Waals complex between thiirane (cyclic C_2H_4S) and a rare gas atom (Ne, Ar, Kr) is easily produced in the supersonic expansion. The position of the rare gas atom with respect to the cycle can be determined by a study of the spectra of various isotopomers (^{13}C, ^{34} S, ^{33}S, isotopic species of neon or krypton). A comparison will be presented between the three complexes containing respectively the neon, argon or krypton atom.

In the case of thiirane-neon complex, a large amplitude motion of the neon atom around the thiirane molecule has been noticed in the spectra, where most of the lines are split into two components. This motion has also been observed in similar complexes (oxirane-Ar, oxirane-Ne) and will be discussed.

P2.4

EXPERIMENTAL HR FTIR AND THEORETICAL STUDIES OF STABILITY OF HYDROGEN CHLORIDE COMPLEXES WITH ETHYLENE AND ACETYLENE

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HR FTIR detailed study on intermolecular interactions in van der Waals dimers between HCl and different molecular species in gaseous phase will be presented. The binding energy of the intermolecular bond is the most important parameter to characterise stability of the dimer. High resolution infrared spectroscopy of binary molecular complexes - hydrogen chloride with acetylene (or ethylene) - were used in this work for determination of the dimers structure and parameters of their potential energy surface. Our measurements mainly concerns rotational structure of HCl stretch spectral band.

Hartree-Fock SCF calculations were performed on the C_2H_4 and C_2H_2 complexes with HCl. Gaussian 98 with the basis set b3lyp/6-311G**(3df, 3pd) was used for structure and energy calculations. Several geometries were considered and optimised. The lowest energy structure was found to be T-shaped with the HCl hydrogen bonded to the π cloud of the unsaturated hydrocarbons as has been shown in the previous studies of these dimers. The hydrogen bond distance was found in the ethylene HCl dimer to be 0.018 Å longer than in the acetylene-HCl dimer.

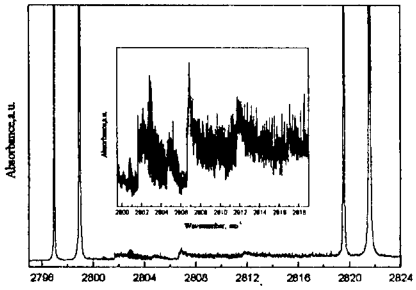

Fig 1. A survey spectrum of gaseous acetylene-hydrogen chloride spectrum.

The rotational spectra of two isotopic species of weakly bonded complexes formed between HCl and ethylene or acetylene have been obtained. The rotational structure of the transition, associated to H-Cl vibration stretch is only partially resolved even at 0.003 cm^{-1} resolution of the spectrometer. This excitation is accompanied by strong vibrational energy migration in van der Waals complex. Vibrational frequency shift with formation of the complex is good visualizasion of complex virbation predissosiation life time. Larger frequency shift of ethylene-HCl complex witch come to 87 cm^{-1}, is defined by the shorter life time compare to acetylene HCl dimer, which shift is 80 cm^{-1}.

The enthalpy of ethylene-HCl complex formation was found to be (9.8 ± 0.5) kJ/mol, it corresponds to (819±40) cm^{-1} value. While the enthalpy of acetylene HCl dimer formation was found to be (6.9 ± 0.8) kJ/mol. This corresponds to (576± 70) cm^{-1}.

CHARACTERISATION OF THE $CH_3F{\cdot}BF_3$ VAN DER WAALS COMPLEX OBSERVED IN THE VAPOUR PHASE.

P2.5

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Using variable-temperature infrared spectroscopy, the vapour phase complexation enthalpy for the Van der Waals complex between CH_3F and BF_3 has been determined to be −16.5(7) kJ mol^{-1}. This value is compared with the results obtained for solutions in liquid argon and in liquid krypton, and with results obtained from ab initio calculations in which the geometry of the complex is optimised using BSSE-corrected potential energy surfaces.

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P2.6

AXIAL AND EQUATORIAL HYDROGEN BONDS IN PENTAMETHYLENE SULPHIDE ··· HYDROGEN FLUORIDE COMPLEX

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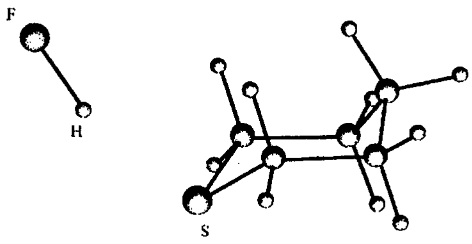
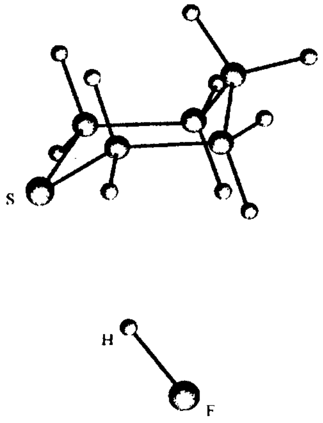
The axial (I) and equatorial (II) hydrogen bond complexes formed between pentametylene sulphide and hydrogen fluoride in a supersonic expansion have been characterised using a Fourier transform microwave spectrometer. The axial form has been found to be the most stable one. The rotational transitions of the parent, $C_5H_{10}\,{}^{34}S \cdots HF$ and $C_5H_{10}S \cdots DF$ species, together with the spectra corresponding to all ${}^{13}C$ species for both forms have been measured. Spectral analysis yielded rotational and centrifugal distortion constants and the parameters accounting for spin (H)-spin (F) and D-nuclear quadrupole couplings. These data are consistent with a C_s symmetry for both conformers: the HF lies in the plane bisecting the CSC angle forming a hydrogen bond to the sulphur atom. Along with the geometry of the axial and equatorial hydrogen bonds, the structure of pentamethylene sulphide subunit has been determined in both cases.

(I)
equatorial



(II)
axial



P2.7

THE ROTATIONAL SPECTRUM OF $(CH_3)_2SiHCl$ USING A FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

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When chlorodimethylsilane, $(CH_3)_2SiHCl$, was discharged in order to search rotational transitions of dimethylsillene, $(CH_3)_2Si$, many strong lines for this parent species appeared. The study of $(CH_3)_2SiHCl$ by the microwave spectrometer were reported in two theses, however, their results had not yet been published.[1,2] The advantages of a Fourier transform microwave (FTMW) spectrometer are high resolution, 2kHz, and high sensitivity comparing with an ordinary Stark modulation microwave spectrometer. Therefore, the rotational transitions were observed in the region of 5 to 20 GHz using a FTMW spectrometer. A 2% sample was diluted in argon and a backing pressure was about 1atm and typical integration was 100 to 500. Three a-type transitions were found near the calculated frequencies based on an estimated molecular structure. These three transitions had hyperfine structures due to the chlorine nucleus in the 20 MHz region. In the addition, each transition has three components due to the internal rotation of the methyl groups in the several 10 kHz region. In order to confirm this assignment other two R-branch transitions, $J = 1 - 0$ and $J = 3 - 2$, and seven Q-branch transitions up to $J = 6$ were observed. However, any c-type transitions were not observed. The rotational spectra of other four isotopic species, ^{37}Cl, ^{29}Si, ^{30}Si, and ^{13}C, were observed in the natural abundance. The substitution structure of $(CH_3)_2SiHCl$ were determined by the obtained rotational constants, r_s(Si-Cl) = 2.0604 (10) Å, r_s(Si-C) = 1.8542 (10) Å, /ClSiC = 108.43 (20) °, and /CSiC = 112.32 (15)°. Using the obtained nuclear quadrupole coupling constants of the chlorine nucleus χ_{bond} and η were obtained as to –35.56 MHz and 0.016, respectively. The ionic character of chlorine and silicon atom was estimated to 65% and this value was agreed with related molecules contained with a silicon atom. Some transitions, $3_{21} - 2_{20}$, $5_{24} - 5_{05}$, etc, have four components due to the internal rotation of the methyl group. The value of the potential barrier V_3 of internal rotation of the methyl group was calculated to be 1710 cal/mol and agreed with those of the related molecules. The values of the almost molecular constants obtained for $(CH_3)_2SiHCl$ using our FTMW spectrometer were nearly one order magnitude better than the previous data.[1,2]

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P2.8

INTERNAL DYNAMICS IN AZETIDINE: A MICROWAVE AND *AB INITIO* STUDY

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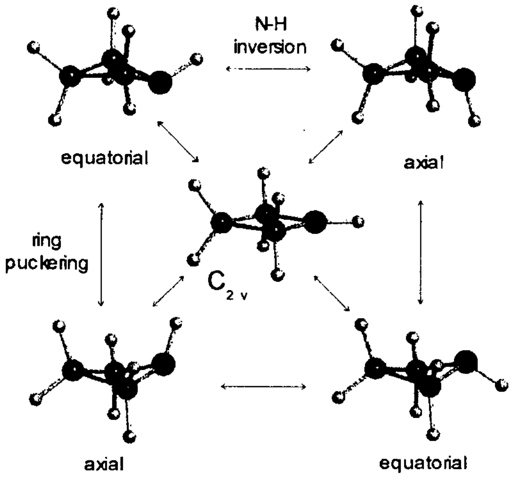
Azetidine has been investigated using Microwave Spectroscopy in combination with *ab initio* computations. The microwave spectrum has been observed in the 8-220 GHz region. The analysis of the rotational spectra has been completed for the ground and first four excited states of the ring-puckering vibration. Rotational transitions exhibit a characteristic doubling originated by tunneling between equivalent conformations. The tunneling splittings show a 9/7 nuclear spin statistical weight effect characteristic for the exchange of three pairs of hydrogen atoms. These intensity effects are an evidence that interconversion between equivalent forms occur through a barrier at the C_{2v} conformation in which the ring atoms and the NH bond are coplanar. The motion responsible for tunneling result from a strong interaction between ring-puckering and NH inversion as predicted from the *ab initio* MP2/6-311+G(d,p) two-dimensional energy surface. The ring-puckering dependence of the rotational and centrifugal distortion constants is only consistent with an asymmetric single minimum potential function for this motion. This result allow us to definitively conclude that azetidine has only one stable form in which the amino group proton is in equatorial position.



ON THE STUDY OF HIGH RESOLUTION VIBRATION-ROTATION SPECTRA OF POLYATOMIC MOLECULES

P2.9

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Methods and Hamiltonian models based on the theorems and results of the Irreducible Tensorial Sets theory were derived which allow one to efficiently analyse complicated modern high resolution vibration-rotation spectra of polyatomic molecules. Derived methods give possibility to correctly take into account different types of intramolecular effects and interactions (e.g., any kinds of accidental resonance interactions). On this base set of computer programs was created.

Derived theoretical methods are applied to analysis of complicated first time recorded high resolution spectra of different types of polyatomic molecules. As the illustration, spectra of D2CO (nine strongly interacting bands ¦Ô2, 2¦Ô4 , 2¦Ô6 ,¦Ô1 , 2¦Ô3 ,¦Ô3 + ¦Ô4 , ¦Ô3 + ¦Ô6 ,¦Ô5 , ¦Ô4 + ¦Ô6), HDO (four strongly interacting bands 3¦Ô1 ,¦Ô1 +¦Ô2 +¦Ô3, 3¦Ô2 + ¦Ô3 ,and 6¦Ô2), D2Se/HDSe (fine rotational structures of more than 100 rotational-vibrational bands in the region of 1200-8000 cm^{-1}), and PH_2D/PHD_2 (pure rotational and fundamental bands) are considered.

P2.10

TUNNELLING OF WATER IN THE DIMETHYL ETHER-WATER COMPLEX.

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The rotational spectrum of the dimethyl ether-water (DME-W) complex has been assigned in a supersonic expansion through millimeter wave absorption spectroscopy. In order to reach the best experimental conditions a mixture of 7% of DME in Ar at a pressure of about 60 kPa was flown over water at room temperature and expanded to about 1 Pa though a pulsed nozzle with a 0.35 mm diameter.

The rotational spectra of the DME ··· H_2O, DME ··· D_2O, DME ··· DOH, and DME ··· $H_2{}^{18}O$ isotopomers have been measured. All rotational transitions were split into two component lines. The magnitude of such a splitting was not significantly influenced by the deuteration of the water molecule, suggesting the doubling to be due to a tunnelling motion of the entire water molecule with respect to DME. A model based on a potential energy surface with four equivalent minima for this motion could account for the experimental evidences.

HYPERFINE LEVEL DEPENDENCE OF PRESSUREBROADENING IN MOLECULAR SPECTRA

P2.11

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Only a small number of papers in the literature deal with the collisional broadening and shift of the hyperfine components of a rotational transition and discuss the dependence of the lineshape parameters on the hyperfine quantum number *F*. Almost all the experimental studies support the absence of any dependence. These were the cases of the J=1-0 rotational line of the symmetric top molecules CH_3Cl [1] and CH_3CN [2,3] and of some rotational transitions of the asymmetric rotor CHF_2Cl [4]. The first experimental evidence of an hyperfine effect was obtained [5] for methyl iodide. In this molecule the iodine nucleus has a nuclear spin I=5/2 and its large nuclear quadrupole produces a well spaced hyperfine structure of the rotational transitions. For the J=4-3, K=3 rotational line in the ground vibrational state a variation of about 20% was observed for pressure broadening.

As far as theory is concerned, the case of a linear molecule perturbed by an atom was discussed by Green [6] concluding that the hyperfine dependence should be negligible. A more general theoretical approach to the problem was given in Reference [7]. For molecules interacting mainly by their dipole moment, it was shown that the hyperfine dependence may be important only for the transitions of symmetric top molecules when *K* is different from 0.

We extend the study to six hyperfine components of the rotational transition J=10-9, Kl=9 in the v_6=1 vibrational state. The apparatus employs an IR-millimeter-wave double-resonance technique, where the IR source is used to populate the v_6=1 level of CH_3I contained in a microwave resonator. By accurately selecting the frequency of the CO_2 laser, only the molecules belonging to a well defined velocity class are pumped into the upper vibrational level and sub-Doppler spectroscopy is obtained. The experimental setup was modified with respect to what described in References [8] and [9] by introducing a detection scheme which allows a gain of a factor 20 in the signal-to-noise ratio [10]. An evident dependence on the *F* quantum number was observed for the pressure broadening coefficient and a very accurate validation of the theoretical model developed in References [5] and [7] is obtained.

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P2.12

EXCITED STATE PHOTOELECTRON SPECTROSCOPY OF MOLECULAR AGGREGATES IN THE GASPHASE

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Small molecular aggregates of aromatic molecules with rare gases, ammonia, carbondioxide, etc. have been investigated by "Excited State Photoelectron Spectroscopy" and REMPI Spectroscopy. Using these methods, the structure of the complexes, the influence of aggregation on ionization potentials and intramolecular vibrations in the ionic aggregate can be evaluated. The photoelectron spectra reveal the distribution of internal energy and dynamic processes in the ionic complexes.

He(I) PHOTOELECTRON SPECTROSCOPY AND ELECTRONIC STRUCTURE OF ALKYLLITHIUM CLUSTERS[1]

P2.13

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The electronic structure of some alkyllithium clusters has been investigated by He(I) photoelectron spectroscopy. Two distinct types of spectra have been observed. This is explained by the different degree of association of the compounds in the gas phase, as determined by the steric demand of the alkyl substituent. From the analysis of the spectra it can be concluded that isopropyl-, *sec*-butyl-, and *tert*-butyl-lithium form only tetramers, while ethyl-, *n*-propyl-, *n*-butyl-, and isobutyl-lithium are mixtures of tetrameric and hexameric clusters in the gas phase. This observation is also in accord with former mass spectrometric investigations.[2–4] The band shapes and intensities are interpreted by a Jahn–Teller distortion of the ionic clusters, which is further examined by *ab initio* quantum chemical calculations. The effect of the substituents and the degree of association on the electronic structure of alkyllithium clusters is clarified.

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P2.14

WHAT TO SEE AND WHAT NOT TO SEE IN 3 PHOTON ABSORPTION: (3+1) REMPI OF HBr AND HCl.

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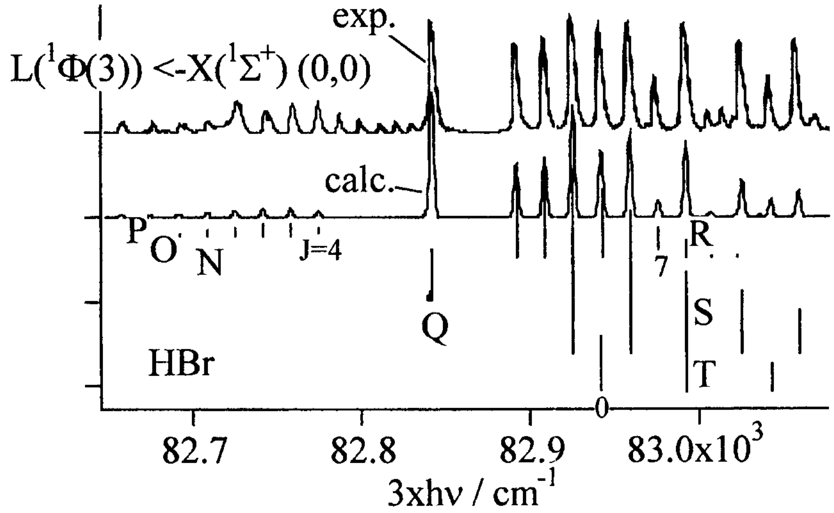
Hönl-London type approximation expressions have been derived for transition strengths of the $\Omega'=0,1,2,3, <- \Omega''=0$ (Σ,Π,Δ and $\Phi <- \Sigma$) three photon transitions for diatomic molecules belonging to Hund's case (a) and intermediate (a)-(b) coupling schemes. These are used to demonstrate what may be seen and what may not be seen in three photon absorption spectra. The forms are used to simulate room temperature (3+1)REMPI spectra of HBr and HCl, for different electronic transitions. The analysis as well as comparison with (2+1)REMPI spectra is used to demonstrate the usefulness of three photon absorption spectroscopy to identify excited states and to derive spectroscopic parameters. Rydberg states, not observed in single or two photon absorption, with band origins 80167 cm^{-1} and 82837 cm^{-1} have been identified and analysed for the first time for HBr. These are assigned as the (0,0) bands of the I $^3\Phi(3)$ and the L $^1\Phi(3)$ states $((\sigma^2\pi^3)5d\delta))$ respectively.



R2PI DETECTION OF THE QUANTUM YIELDS OF I($^2P_{1/2}$) AND I($^2P_{3/2}$) IN THE PHOTODISSOCIATION OF C_2F_5I, n-C_3F_7I, i-C_3F_7I and CH_3I.

P2.15

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The photodissociation of the perfluoroalkyliodides has been the subject of many studies during the last decades. The interest in these molecules comes from their use as precursors of excited iodine atoms ($^2P_{1/2}$) in the active medium of the photodissociation iodine laser. Also the effect of different substituents on the photodissociation dynamics is of interest. A particularly interesting substance among the perfluoroalkyliodides is n-C_3F_7I which has been used as a reference source with unity yield of I($^2P_{1/2}$) atoms in a series of measurements of the excited atom yield in the photodissociation of iodine-containing molecules.

In this work resonant two-photon ionization R2PI has been applied to the measurements of the quantum yields φ of iodine atoms in the fine structure states $^2P_{1/2}$ and $^2P_{3/2}$ arising in the UV-photodissociation process (λ=266 and 355 nm) of the perfluoroalkyliodides C_2F_5I, n-C_3F_7I and i-C_3F_7I as well as of methyl iodide CH_3I (λ=266 nm). The results obtained show that the quantum yield φ_{266}^* of the excited state atoms I($^2P_{1/2}$) in the photodissociation process of the perfluoroalkyliodides differs noticeably from unity which has previously been assumed or measured for these molecules.

P2.16

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF MASS SELECTED IONIC COMPLEXES COMPOSED OF PHENOL OR PROTONATED PHENOL CATIONS AND NEUTRAL LIGANDS

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Ionic hydrogen bonds are of special interest not only because they are intermediates of proton transfer reactions but also because of their fundamental importance in many areas of physics, chemistry and biology. Larger clusters consisting of an ion and several surrounding neutral ligands are model systems to study microsolvation processes and to estabilish the bridge between the gas and condensed phases.

In this contribution we would like to present new results on phenol (Ph^+) and protonated phenol (PhH^+) cations solvated by n neutral ligands (L=He/Ne/Ar/N_2, n=1-7) obtained by infrared photodissociation (IRPD) spectroscopy in a tandem mass spectrometer. The method combines high sensitivity (single ion counting with 100% detection efficiency, background free) with high selectivity (double mass selection).

IRPD spectra of Ph^+-L_n and PhH^+-L_n have been recorded in the spectral range of the O-H stretch vibrations. The observed intensities and frequency shifts as a function of L and n give valuable insight into the binding mechanism and the cluster growth (structure, binding energy, existence and relative stability of isomers).

The most stable Ph^+-Rg dimers (Rg=He/Ne/Ar) have proton-bound equilibrium geometries. This observation represents the first aromatic ion-Rg dimer where the Rg atom does not bind to the π-electron system of the aromatic ring.[1] This result could be obtained by producing the complexes in an electron impact ionisation source[1] rather than by resonance enhanced multiphoton ionisation of the neutral precursor.[2] The frequency shifts (and thus the binding energies) scale with the polarizabilities of the Rg atoms, indicating that induction interactions dominate the attraction. The intermolecular bond in Ph^+-N_2 is much stronger due to the additional charge-quadrupole interaction. In the case oh Ph^+-Ar also the second, less stable π-bound isomer could be observed.[1,2]

The spectra of PhH^+-L_n (L=Ar/N_2) show three absorptions in the O-H stretch region that are attributed to two isomeric forms of protonated phenol: one corresponds to protonation at the O atom (giving rise to symmetric and antisymmetric O-H stretch modes) and one corresponds to protonation at the aromatic ring (giving rise to only one O-H stretch band). Complexation occurs first at the acidic O-H bond(s) and subsequent ligands occupy less favorable binding sites. This interpretation is supported by the frequency shifts observed upon sequential complexation, as well as the different binding energies of the two isomers deduced from the different fragmentation branching ratios.

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IONIZATION ENERGY OF 4-AMINOBENZONITRILE AND VIBRATIONAL LEVELS OF 4-AMINOBENZONITRILE CATION DETERMINED BY MASS-ANALYZED THRESHOLD IONIZATION SPECTROSCOPY

P2.17

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Mass-analyzed threshold ionization (MATI) and two-color resonant two-photon ionization (2C-R2PI) methods were used to investigate the ionic properties of 4-aminobenzonitrile (4ABN). The adiabatic ionization energy (IE) of 4ABN was measured to be 66 494 ± 4 cm^{-1} by the MATI spectroscopy and 66 492 ± 7 cm^{-1} by the 2C-P2PI spectroscopy. The vibrational features of the 4ABN cation were also recorded by the MATI spectroscopy. Experimental results show that most of the active motions are related to in-plane ring vibrations. We have also performed ab initio and density functional theory calculations for predicting the IE and vibrational frequencies. It was found that the B3PW91/6-311+G** calculations only underestimated the IE by about 0.18 eV, which is equivalent to a deviation of 2.1%.

Low Temperature Spectroscopy

-Matrix Isolation
-LNG Spectroscopy
-Solid State

FTIR SPECTRA OF LIQUID ARGON / LIQUID OXYGEN, AND LIQUID NITROGEN / LIQUID OXYGEN MIXTURES: EVIDENCE FOR THE EXISTENCE OF THE 1:1 BONDED SPECIES AR·O_2, AND N_2·O_2.

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The infrared spectra of liquid phase argon/oxygen (78-121K), krypton/oxygen (78-140K) and nitrogen/oxygen (78-123 K) mixtures are reported. Superposed on the broad, collision induced monomer bands, for the Ar/O_2, the Kr/O_2 and the N_2/O_2 mixtures weak bands, proving the existence of 1:1 species Ar·O_2, Kr·O_2 and N_2·O_2, were observed. Using spectra recorded at different temperatures, for all complex species, information on the relatively stability was determined.

P3.2

A CRYOSPECTROSCOPIC STUDY OF THE OLIGOMERS OF DEUTERIUM CHLORIDE IN LIQUID ARGON, LIQUID KRYPTON AND IN LIQUID NITROGEN

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The infrared spectra of HCl and DCl dissolved in liquid argon, liquid krypton and liquid nitrogen are discussed. In analogy with the results obtained for solutions containing only HCl, in the spectra of the solutions containing DCl, new bands proving the existence of oligomeric species $(DCl)_x$ were observed. The analysis of the spectra recorded from solutions in which the mole fraction of HCl and DCl were varied between 1.0×10^{-5} and 2.5×10^{-3}, show that these bands must be assigned to dimer, trimer and tetramer species.

VIBRATIONAL SPECTRA AND RELATIVE STABILITY OF THE VAN DER WAALS COMPLEXES FORMED BETWEEN METHYLENECYCLOPROPANE, BF_3 AND HCL: AN FTIR AND DFT STUDY

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The formation of weak molecular complexes between methylene-cyclopropane (MeCP), BF_3 and HCl dissolved in liquid argon and in liquid nitrogen has been investigated using infrared spectroscopy. For both the solutions with BF_3 and HCl, evidence was found for the formation of a 1:1 complex in which the Lewis acid binds to the C=C double bond, while at higher concentrations of HCl and BF_3, also weaker bands due to different 1:2 complexes were observed. From spectra recorded at different temperatures between 90 and 130K, the complexation enthalpies for MeCP·HCl and MeCP·BF_3 were determined to be –9.9(3) kJ mol^{-1} and –10.7(3) kJ mol^{-1}, respectively, while the corresponding value for the 1:2 complex with HCl, MeCP·$(HCl)_2$, was determined to be –14.6(4) kJ mol^{-1}. Structural and spectral information for the 1:1 and the 1:2 complexes was obtained from DFT calculations at the B3LYP/6-311++G(d,p) level. Using Free Energy perturbation Monte Carlo simulations to calculate the solvent influences, and statistical thermodynamics to account for zero-point vibrational and thermal contributions, from the experimental complexation enthalpies the complexation energy for the MeCP·HCl, MeCP· $(HCl)_2$ and for MeCP·BF_3 were estimated to be –16.9(12), -28.7(14) and –16.0(10) kJ mol^{-1}, respectively. These numbers are compared with single point energies calculated at the MP2/aug-cc-PVTZ level.

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P3.4

CONFORMATIONAL STABILITIES OF $CH_2=CHSi(CH_3)_nX_{3-n}$ (X = F AND Cl) FROM VARIABLE TEMPERATURE FT-IR SPECTRA OF RARE GAS SOLUTIONS

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We [1-4] have been determining the conformational stability of a number of organosilicon molecules of the general formula CH_2CHSiX_2Y where X = H, Cl, F, Br and Y = H, Cl, F, Br, CH_3. We have shown that the data obtained from the temperature dependent infrared spectra of noble gases can provide definitive data for the determination of the conformational stabilities of these molecules. As an example, from the microwave study of methyl vinyl silane no conclusion was drawn on the conformational stability where from the vibrational study [1,2] the *cis* conformer was proposed to be the more stable rotamer. However, from the temperature study of the infrared spectrum of methyl vinyl silane in the krypton solution, the *gauche* conformer was determined to be the more stable rotamer with an enthalpy difference of 133±11 cm^{-1} (1.59±0.13 kJ/mol).

As a continuation of these studies we have investigated the conformational stabilities of the corresponding compounds when the hydrogen atoms are replaced by fluorine or chloride atoms. Variable temperature (-55 to -100°C) studies of the infrared spectra between 3500 and 400 cm^{-1} of methyl vinyl difluorosilane, $CH_2=CHSiF_2CH_3$, dissolved in liquid xenon has been recorded. From these data, the enthalpy difference has been determined to be 83±11 cm^{-1} (0.99±0.13 kJ/mol), with the *gauche* conformer the more stable rotamer. Similar studies in both liquid xenon and krypton have also been carried out for dimethyl vinyl fluorosilane, $CH_2=CHSiF(CH_3)_2$. From the xenon and krypton data, the enthalpy differences have been determined to be 53±9 cm^{-1} (0.64±0.10 kJ/mol) and 44±7 cm^{-1} (0.53±0.09 kJ/mol), respectively, with the *gauche* conformer being the more stable form. However, in the spectrum of the solid, the *trans* conformer is the stable rotamer. Similar studies have also been carried out on the corresponding chlorides.

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THE RADICAL CATION OF PIPERAZINE: AN EXPERIMENTAL AND COMPUTATIONAL STUDY

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In previous studies we have investigated the radical cations of the amines N,N-dimethylpiperazine[1] (DMP) and 1,4-diazabicyclo[2.2.2]octane[2] (DABCO). In the present communication we report experimental and computational studies of the piperazine radical cation.

The electronic absorption (EA) and resonance Raman (rR) spectra of the piperazine radical cation, produced by γ-radiolysis in a Freon glass, were recorded.

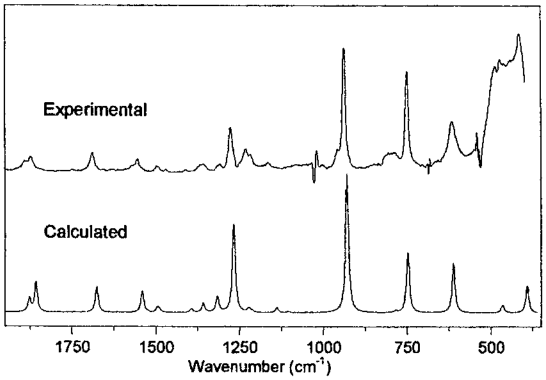

Fig. 1 – Experimental and calculated vertical rR spectra of the piperazine radical cation

From DFT calculations it was found that the lowest energy geometry for the radical cation ground state corresponds to a C_{2h} chair conformer with the N-H bonds oriented axially, similarly to the DMP radical cation. The absorption band at 550 nm was assigned to the $1^2A_g \rightarrow 1^2B_u$ electronic transition. The EA spectrum and rR intensities were calculated by means of wavepacket propagation techniques, employing both adiabatic and vertical approaches.[1] The spectra calculated using the vertical approach give good agreement with the experimental ones (see Fig. 1), while those predicted by the adiabatic method are far off. This implies substantial anharmonicity of the 1^2B_u potential energy surface, in line with our observations for the DMP radical cation.[1] It is also concluded that in the low temperature matrix only the lowest energy C_{2h} chair conformer contributes to the spectra observed.

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P3.6

MATRIX ISOLATION STUDIES OF H_2S/SO_2 MIXTURES IN RARE-GAS MATRICES

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Reactions of SO_2 have been studied in mixed $H_2S/SO_2/Rg$ matrices. The matrix samples were photolysed by UV irradiation producing a hydrogen atom and SH radical. In annealing of UV irradiated matrices, a number of new strong IR absorptions were observed. Simultaneously, the SO_2 absorptions disappear suggesting reactions between SO_2 and the photofragments. These observations suggests that hydrogen atoms react with SO_2. Possible candidates for the new absorbers are, for example, isomers of HSO_2, which to our knowledge, have not been characterised in rare-gas matrices so far. To aid experimental investigations, ab initio calculations were carried out for some sulphur and oxygen containing molecules.

Equilibrium structures, energies and vibrational wavenumbers were studied at the MP2/6-311++g(2d,2p) level. In our study, we focused our attention to the three isomers HSO_2, trans-HOSO and cis-HOSO. Computationally, HSO2 is considerably higher in energy than the HOSO isomers, the cis-HOSO being the global minimum.

Comparison between computational wavenumbers of various HOSO isomers and experimental wavenumbers suggest the formation of HSO_2 isomers upon annealing of matrices containing SO_2 and hydrogen atoms.

VIBRATIONAL SPECTRA AND STRUCTURES OF METAL (Ti, Ni, Pd) MONONITROSYL COMPLEXES. AN IR MATRIX ISOLATION AND DFT STUDY

P3.7

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The infrared spectra of nickel, palladium and titanium mononitrosyl isolated in solid argon at low temperature have been reinvestigated (1, 2). Two kinds of mechanisms of reactions metal-NO have been observed :

In the Ni + NO and Pd + NO experiments, concentration and photochemical studies demonstrate the existence of two isomeric forms of NiNO and only one isomeric form of PdNO with a bent structure. In the NiNO complex case, analyses of the $^{58}Ni/^{60}Ni$, $^{14}N/^{15}N$ and $^{16}O/^{18}O$ isotopic effects indicate that a first form has an end-on bent configuration (as with palladium), and a second form has a cyclic structure, in which the NO ligand is significantly more perturbed. Reversible conversion is achieved by photo selective UV-Visible excitation.

In the Ti + NO experiments, no side-bonded TiNO form has been observed and insertion reaction doesn't need any appreciable activation energy. All three modes of the N-Ti-O insertion product are detected. Comparisons between the Ni+NO, Pd+NO and Ti+NO systems are presented.

Density Functional calculations of the geometrical, electronic and vibrational properties(2,3) of these isomers are also presented and compared to the experimental values. Isomerization energies have been estimated.

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P3.8

PHOTODISSOCIATION OF VIBRATIONALLY EXCITED HCL IN MATRIX

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Photochemical reactions in the condensed phase are strongly influenced by the surrounding and this multidimensional problem is difficult to treat. A considerable effort has be invested in modelling the cage effect for the escape of the H atoms in the photodissociation of the HCl molecules in an fcc rare gas lattice which is considered as a benchmark system. Experimentally the excitation from v=0 of the bound X state to the repulsive A state requires tuneable radiation in the range of 180 to 150 nm which is difficult to provide, the small Frank-Condon regime from v=0 limits the range of available kinetic energies of the H atoms and contributions from monomers, dimers and multimers are difficult to separate. In addition the predicted dependence of the dissociation efficiency on HCl orientation should be studied by preparing different rotational states. All these points are solved by a 2-step-photodissociation.

The first step a vibrational excitation into the v=1 to v=4 levels of the electronic ground state serves as a preselection which is used for example to discriminate between monomeric and polymeric isolated species of HCl or to excite rotational side bands. In a subsequent second step we perform the photodissociation from this different vibrational levels into the repulsive state, using UV-light.2 tuneable dye-lasers serve as excitation sources. The output of the first dye laser is shifted in a hydrogen filled Raman cell into the near infrared at 3.47, 1.8, 1.2 and 0.9 um for the IR-preexcitation of v=1,2,3 and 4 respectively. Control of the vibrational population is carried out by monitoring the v -> v-1 fluorescence. The output of a frequency doubled dye laser is used for the electronic excitation.

Fluorescence of the formed RgCl (Rg = Ar, Kr, Xe) exciplexes excited with an exciplex laser monitors the degree of dissociation. Dissociation efficiencies for the different vibrational levels and for varying the dissociation wavelength are reported and related to molecular dynamics simulations of the cage effect. Fine structure in the rotational R(1) and R(2) branches is observed and discussed in context to the interaction with the matrix environment. Dissociation efficiencies for the different rotational levels are presented and discussed.

P3.9

CO-CONDENSATION OF CHROMIUM WITH CO IN ARGON AND NITROGEN MATRICES: FTIR AND DENSITY FUNCTIONAL STUDIES

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First row transition metal carbonyls have been subject of numerous experimental and theoretical investigations because of their key role in modeling homogeneous and heterogeneous catalytic processes.

Reaction products of Cr with CO_2 (1,2) and molecular and/or atomic nitrogen (3,4) have been extensively studied in the past, while the characterization of Chromium carbonyls is far from complete.

In the frame of a systematic research on complexes involving metals of catalytic interest, a FTIR study has been undertaken on complexes of Cr atoms with CO both in argon and nitrogen cryogenic matrices. The generation of Cr monocarbonyl in argon excess has been proposed long ago (5). Our data confirm its formation. In addition, the experimental evidence is given of a dicarbonylic complex.

The FTIR spectra of chromium vapor in neat nitrogen matrices doped with ^{12}CO appear totally different from those obtained in argon suggesting the genesis of mixed chromium CO/N_2 species. Isotopically labeled measurements helped the assignment. Density Functional calculations on vibrational spectra of many stable aggregates $Cr(CO)_x(N_2)_y$ (x, y = 0, 1, 2) provided a valuable support for the assignment.

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P3.10

INFRARED SPECTRA OF CO IN RARE GAS MATRICES

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Carbon monoxide in rare gas matrices is one of the simplest systems for matrix isolation spectroscopy. Interpretation of the observed spectra is, however, not straightforward; the CO spectra contain several components although CO has only one vibrational mode in the mid-infrared region. The observed spectral features are different for each matrix medium. The fact that the spectral features depend strongly on the various experimental parameters makes it difficult to interpret the spectra. To overcome those difficulties and to understand the nature of CO in rare gas matrices in detail, we have reinvestigated infrared spectra of carbon monoxide in Ar, Kr, and Xe matrices at cryogenic temperatures.

By FTIR spectroscopy the infrared spectra have been recorded in the region from 1800 to 4000 cm^{-1} over a wide range of experimental conditions with a certain spectral reproducibility. Several observations have shown that the absorption profile in all the three matrices can be attributed mainly to three components, namely, A, B, and C, in increasing order of wavenumber. On the basis of experiment with samples of various concentration of CO, the three peaks observed in all the matrices are assigned as follows: peak A to the CO monomer which cannot librate in the matrices, peak B to the CO monomer which can librate, and peak C to the CO dimer which can also librate.

The present assignments are different partly from those reported previously in literature [1]. The differences in the spectra among the three matrix media can be attributed to the differences of peak intervals. This dependence of the peak intervals as well as center position on the matrices will be discussed.

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STRUCTURAL ORDER AND VIBRATIONAL RELAXATION OF PHENYLACETYLENE IN LIQUID SOLUTIONS AND FROZEN MATRICES AT LOW TEMPERATURES.

P3.11

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Raman spectra of the $\nu_s(C\equiv C)$ stretching mode of phenylacetylene dissolved in benzene, methylcyclohexane, and acetonitrile and the $v_8(C—C\equiv N)$ mode of acetonitrile have been recorded in liquid solutions at room temperature and in solid state frozen matrices at 77K as a function of concentration. The spectra at low temperature reveal spectacular changes in comparison with those observed in liquid solutions. One of the goals of these measurements for example of phenylacetylene dissolved in acetonitrile was to identify the mechanism of vibrational relaxation in the full range of temperatures with a special emphasis on the range around the phase transitions occurring between 183 to 218K. We have found that bandbroadening of the $\nu_s(C\equiv C)$ mode of phenylacetylene in acetonitrile solutions is dominated by pure dephasing in the whole temperature range. For temperatures between 77 to around 125K the vibrational energy relaxation T_1 makes not negligible contribution for the peak at 2116 cm^{-1} ascribed to the $\nu_s(C\equiv C)$ oscillator which is not involved in H-bond. For the $\nu_s(C\equiv C)$ oscillators at 2015 and 2110 cm^{-1}, which are engaged in H-bond, the T_1 relaxation is negligible in the whole temperature range. The orientational relaxation resulting from the rotations of the whole molecules are also negligible. The mechanism of vibrational dephasing of the $\nu_s(C\equiv C)$ oscillator involved in H-bond, which is reflected by the spectacular bandbroadening of about 6 cm^{-1} around phase transitions, comes from the coupling with the bending mode $v_8(C—C\equiv N)$ of acetonitrile. The oscillator at 2116 cm^{-1} shows much less spectacular change around phase transitions, while the oscillator at 2110 cm^{-1} is independent of the phase transitions between 183 and 218K. We have found that the $\nu_s(C\equiv C)$ vibration of phenylacetylene in acetonitrile shows approximately Arrhenius behaviour with a thermal activation energy of 310±108, 190±74, and 112±34 cm^{-1}, respectively. The activation energy for the peak at 2105 cm^{-1} covers the range of the $v_{16a}(B_2)$ vibration of the phenyl ring in phenylacetylene at 349 cm^{-1}and the bending mode $v_8(E)(C—C\equiv N)$ at 375 cm^{-1} in acetonitrile, respectively. The activation energy for higher frequency peaks cover the range of transitional and vibrational optic phonons at much lower energies that v_8 and v_{16} modes. Spectra were recorded at room temperatures and at77K in a liquid nitrogen bath cryostat. The samples at 77K were prepared by slow freezing with temperature going down gradually. The possible explanation of the experimental results is the existence of three different phases in frozen matrices: glassy, isotropic (similar to that in liquid phase) and crystalline ones. The results show that phenylacetylene solutions and pure phenylacetylene have properties being in-between those of isotropic liquids, glassy and crystalline solids and the mechanisms of vibrational dephasing in liquid and solid phenylacetylene solutions for some concentrations are similar and typical for isotropic liquids. On the other side may be observed splitting of the $\nu_s(C\equiv C)$ band and the change of the depolarisation ratio with temperature and concentration indicating anisotropic properties typical for crystals.

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P3.12

MATRIX ISOLATION AND THEORETICAL STUDIES OF TERNARY COMPLEXES BETWEEN NITROUS ACID, WATER AND AMMONIA

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Nitrous acid is a very important species in atmospheric chemistry. It acts as a source of hydroxyl radicals. Molecular complexes formed between HONO and water molecules are very interesting, because water is one of products of the nitrous acid decomposition reaction. On the other hand the reaction between HONO and ammonia is a possible pathway for interconversion of nitrogen oxides to molecular nitrogen. Here we present the experimental and theoretical study of the binary H_2O...HONO and ternary NH_3...H_2O...HONO complexes. The study of the NH_3..HONO system was reported earlier[1].

The infrared spectra of binary and ternary complexes between water, nitrous acid and ammonia molecules isolated in argon matrices have been studied by FTIR spectroscopy. Theoretical studies of the structures and spectral characteristic were carried out at the B3LYP level using 6-311++(2d,2p) basis set.

Perturbed HONO, water and ammonia vibrations were observed both for binary H_2O...HONO and ternary NH_3...H_2O...HONO complexes. Experimental results show that addition of ammonia to H_2O...HONO heterodimers leads to formation of ternary H_3N...H_2O...HONO complex in which water molecule acts as proton donor for ammonia and proton acceptor for HONO molecule. The interaction between nitrous acid and water is strongly modified by the presence ammonia molecule; the OH stretching vibration of HONO molecule is shifted from 3322cm^{-1} for H_2O...HONO complex to 2819.2cm^{-1} for ternary complex.

The computational results confirmed that in the most stable ternary complex water interacts both with nitrous acid and ammonia. The structure and the calculated spectral parameters are in very good agreement with experimental data. Theoretical studies demonstrate also the stability of the two other ternary complexes. In the first one water is attached to oxygen atom of the OH group in H_3N...HONO complex. In the less stable ternary complex water is bonded to the terminal oxygen atom of HONO in H_3N...HONO complex.

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INFRARED MATRIX ISOLATION STUDIES OF FORMHYDROXAMIC ACID

P3.13

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Hydroxamic acids have exhibited many interesting facets of chemistry since first reported[1]. They are intimately associated with iron transport phenomena[2]. Many hydroxamic acids show fungicidal, antimalarial and antibacterial activities and thus find therapeutic applications[2,3]. Both hydroxamic acids and their N-substituted derivatives serve as bidentate ligands toward many metal ions[2,4].

In spite of these interesting properties, hydroxamic acids are one of the less well characterized classes of organic compounds. Their spectroscopic properties, behaviour in binary interactions or even assignment of the correct structure remain still unsolved problems. Difficulties are connected to the facts that hydroxamic acids are not stable above their melting point, they are not soluble in non polar solvents and the tautomeric form depends on the polarity of the environment.

We present the results of the infrared studies of formhydroxamic acid isolated in solid argon. The infrared spectra of HCONHOH/Ar, HCONDOD/Ar and $HCO^{15}NHOH/Ar$ matrices show that the molecule of formhydroxamic acid exists as the *keto-* tautomer with intramolecular hydrogen bond in solid argon. In order to determine proton donor and proton acceptor properties of the formhydroxamic acid molecule several different complexes of this compound were examined. The spectra of $HCONHOH-H_2O$, HCONHOH-HCl systems in argon matrices have been recorded. The strength and the type of the interaction in those complexes are discussed.

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P3.14

A MATRIX ISOLATION FTIR STUDY OF SULFURIC ACID AND ITS MOLECULAR COMPLEXES WITH MOLECULES OF ATMOSPHERIC INTEREST.

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Sulfuric acid is a major component of atmospheric aerosols and is involved in many reactions of environmental importance. The present study employs the method of "Matrix Isolation" i.e. isolating the molecules at high dilution in solid rare gases at cryogenic temperatures, to study, by FTIR the sulfuric acid molecule, its deuterated isotopomer and its interactions with various small molecules of atmospheric interest, such as H_2O, CO, HCl, N_2, NO (and $(NO)_2$. The spectroscopic observations are compared to available theoretical computations. The results yield structural information and are sometimes surprising. Such, for example, is the case for the most important complex studied, the 1:1 complex of H_2SO_4 and H_2O. It is this interaction which is they key step in the process leading from a *molecular complex* to the *solvated ionized molecule*. The experimental and theoretical results for this complex are in conflict. Only the comparison with a model compound ($(CH_3)_2SO_2$) leads an unexpected conclusion which seems to contradict chemical intuition.

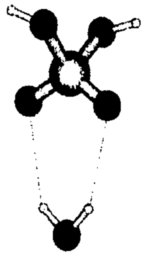

Fig. 1 – The $H_2SO_4 \ast H_2O$ molecular complex

FTIR SPECTRA OF MATRIX ISOLATED PYRUVIC ACID

P3.15

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This work reports part of the ongoing investigation of structure and spectra of biologically active and conformationally flexible compounds isolated in low temperature inert gas matrices resulting from the collaboration between the matrix laboratories of Coimbra and Kharkov.

The subject of this study is pyruvic acid, CH_3-CO-COOH. This compound plays a fundamental role in the regulation of biological activity in the human body. Pyruvic acid has many common features with aminoacids which we have studied previously [1]. Like natural aminoacids it is an alpha-substituted carboxylic acid, which we hope will be of help in developing a reliable transferable molecular force field for these closely related molecules. Pyruvic acid is also a conformationally flexible molecule and, like aminoacids, it is also prone to decomposition. These features make this compound difficult to be studied experimentally both in the gaseous phase and in matrices. To our knowledge only one experimental study has been reported on the matrix isolated pyruvic acid [2]. In that study several impurities were found to be present in the samples, like water, carbon dioxide and acetic acid.

In the current study we have succeeded to obtain the experimental spectra of pyruvic acid isolated in argon matrix with better degree of purity than reported before. In particular, carbon dioxide and acetic acid, which are products of photodecomposition of the studied compound, were absent in our spectra. The matrix spectra are analyzed regarding the presence of different conformers in the matrices and dimerization. Comparison with *ab initio* calculated spectra is provided.

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Spectroscopy of New Materials

VIBRATIONS IN GRAPHITIC MATERIALS: THE MOLECULAR APPROACH

P4.1

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A variety of new carbon based materials, ranging from films of amorphous carbons, to diamond-like carbon (DLC), from fullerenes to carbon nanotubes, have recently received great attention by the scientific community, both from the view points of the basic research and in the perspective of several possible technological applications.

Since the different macroscopic properties (e.g. strength, friction coefficient, conductivity...) of these materials are intimately related to their structure on atomic scale, reliable methods for the structural characterisation and development of structure/property relationships are required.

In this field vibrational spectroscopy, and mostly Raman spectroscopy, has been widely used. In particular Raman spectra of graphitic compounds containing structural disorder of various kinds and amounts have been used for structural characterisation. However, in many cases, only qualitative information have been obtained, based on empirical spectral correlations.

A quantitative discussion of the Raman spectra of graphitic materials must be necessarily based on reliable vibrational dynamical calculations and on band intensity analysis. To this aim an empirical force field has been developed that allows to treat in a coherent, consistent way the dynamical problems of polycyclic aromatic hydrocarbons (PAH) of any size and graphite. In this approach PAH molecules play the role of molecular models which mimic finite size sp^2 domain (graphitic domains) confined by structural disorder in the real materials. Experimental Raman spectra of a variety of PAH of recent synthesis, with well defined structure and size, allow a direct check of the reliability of the calculations. In this way it is possible to establish precise relationships between Raman spectra of PAH molecules and graphite, in terms of vibrational frequencies and with the help of the explicit description of normal modes of vibrations.

Moreover, Quantum Chemical Density Functional Theory calculations have been applied to the case of some PAH of medium size: the results obtained are of great help in understanding how and to what extent Raman Intensities are affected by the confinement, by the symmetry and by the size of the sp^2 domains. These results make possible to give a quantitative estimate of the amount of structural disorder from Raman spectra of the real materials.

Since Raman Intensities are intimately related to the electronic structure, this study lays the background for a further discussion of the effect of confinement on the properties of conjugated; electrons in sp^2 domains.

P4.2

STRUCTURAL AND VIBRATIONAL CALCULATIONS OF FULLERENES

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At present over twenty stable fullerenes Cn have been identified, with n varying from 60 to 96, and also smaller fullerenes like C36 or even possibly C20. After the first wave of the computations of C60 and C70, the research interest has been shifted towards higher and also smaller fullerenes. All the areas will be surveyed accordingly. The computations employ all the available quantum-chemical methods and also some statistical-mechanical approaches. Quantum chemistry has especially been important in understanding higher fullerenes. Elucidation of their structures has entirely been based on the isolated-pentagon-rule (IPR) conjecture, using the topologically generated patterns. The lowest IPR stoichiometry which allows for a structural multiplicity is n=76, however, the case is controlled by a Jahn-Teller effect. Anyhow, beyond n=76, isomerism of the IPR structures should generally play a role in observations. In fact, several such mixtures of fullerene isomers have been computed and an agreement with experiments found, for example: C78, C80 (though experiment has discovered only one C80 species so far), C82 (at present at least two C2 isomers confirmed experimentally), C84, C86, and C88. The thermodynamic computations have clearly shown that temperature effects are essential in understanding higher fullerenes. The inter-isomeric separation energies are certainly important and represent a starting point, nevertheless, they alone cannot predict the relative stabilities of the IPR isomers at elevated temperatures. As the temperatures reached in fullerene syntheses are high, entropy contributions can even over-compensate the enthalpy terms. C90 and C92 are the newest IPR systems submitted to the comprehensive computations. In addition to pristine fullerenes, computations of fullerene derivatives will be surveyed, too. In all the systems considered the computations have supplied structural and vibrational data directly applicable to interpretations of experiments.

EXTERNAL HEAVY-ATOM EFFECT ON THE FLUORESCENCE OF FULLERENES

P4.3

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Fullerenes are very interesting molecules from several points of view. The photophysical and photochemical properties of the most abundant fullerenes, C_{60} and C_{70}, have been the subject of numerous studies[1,2]. It was namely established that intersystem crossing (ISC) is the dominant decay channel for the excited singlet state, the quantum yield of triplet formation being very close to unity. More recently, several addition derivatives were also studied[3].

The external heavy-atom effect is known to be due to enhanced intersystem crossing. It is thus of interest to study the effect of heavy-atoms on the excited-state dynamics of compounds whose ISC is intrinsically efficient[4].

In this contribution, a new kinetic model for the external-heavy atom effect on fluorescence in fluid and rigid solutions will be presented. The application of this model to experimental results, yielding ISC rate constants of the perturbed compounds and other parameters, will be next discussed.

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P4.4

GENERATION AND INFRARED SPECTROSCOPIC CHARACTERIZATION OF FUNCTIONAL GROUPS ON MULTIWALLED CARBON NANOTUBES

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With their high aspect ratio, small diameters, mechanical strength and unusual electronic properties, carbon nanotubes (CNTs) are a unique material whose potential is still being explored. It is well known that the functionalization of the end of the opened CNTs is quite easy because of the high reactivity of the dangling carbon bonds [1]. In contrast to the open tube ends, the side walls of CNTs by virtue of their aromatic nature possess a chemical stability akin to that of the basal plane of graphite. Herein, we report the spectroscopic study of covalent modifications of multiwalled carbon nanotubes to generate functional groups on their side walls.

CNTs were synthesized by the catalytic method where in nitrogen stream acetylene was decomposed on well-dispersed Co particles supported on mesoporous silica [2]. Following the modification resulted in during the reaction diffuse reflectance IR spectroscopy was applied. In order to achieve sufficient signal-to-noise ratio 5 w% of CNTs was used in KBr matrix. To generate different functional groups on CNTs, acylation reactions seemed to be the best choice with oxalyl-chloride, thionyl-chloride, benzoyl-chloride and chloroacetyl-chloride reagents. The reactions took place in CCl_4 in the presence of $AlCl_3$ as a Lewis-type catalyst. The reaction was carried out either in a beaker at atmospheric pressure or at higher pressure in autoclave. The other type of reaction used was a cyclic addition of diethyl-bromomalonate in order to form two ester groups attached to the side walls via a cyclopropane-like ring.

Assuming the perfect graphitic structure of the covering shell of a CNT, theoretically the acylation reagents are not able to react with CNTs. However, the outer surface of the CNTs produced by catalytic method contains several defects, unsaturated, but not aromatic parts. Consequently, during the acylation C=O bonds can be formed. As an experimental proof, in the IR spectra of materials obtained after the reactions a small amount of C=O band was detected in the 1600-1800 cm^{-1} region depending on the reactant. Using diethyl-bromomalonate as reactant in the cyclic addition the functionalization occurs very easily forming two ester groups via a cyclopropane ring on the outer surface. In the IR spectra of materials after the reaction bands appear in the region of 1300-1650 cm^{-1} attributed to the ester-groups and the ethyl-groups formed.

In summary, these studies demonstrate that CNTs can be selectively modified using well-defined covalent chemistry to yield a wide range of functionality.

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RESONANCE ABSORPTION SPECTRA OF COMPOSITES CONTAINING METAL COATED NANOPARTICLES

P4.5

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In recent years under development of new nonlinear materials and effective emitters considerable attention has been given to metal nanoparticle systems due to their unique properties close to plasma resonance frequencies [1]. At some preparation stages heterogeneous particles containing metal can arise. Their optical characteristics need to be studied in additional.

In the case of low particle volume concentration *c* composite resonance absorption in the visible is determined by plasmon modes of single particles. Then extinction coefficient of a composite β=0,75cQ/R, where Q is a particle extinction efficiency factor. Based on the rigorous solutions of the light diffraction problem for a coated sphere [2] we have investigated the plasmon absorption resonance features for compound particles type of metal-dielectric and metal-metal (various combinations of Ag, Au, Cu). The external particle radius R has been extended from 5 to 100 nm.

The size dependence of metal core optical constants has been calculated in the framework of the limitation of electron mean free path model suggested by Kreibig. We have also modified this model for metal-coated spheres [3].

It was founded that a spherical nanoparticle with a metal shell and a dielectric core has two plasmon resonance peaks in extinction spectra associated with electron density oscillations at the external and the internal borders of a metal shell. In the range R up to 10 nm spectral positions of the peaks in contrast with absolute magnitudes in maxima depend only on a core volume fraction p and don't depend on a shell thickness. As p increases from 0 to1 an external and an internal plasmons shift to low and high frequency regions respectively. There is a possibility to control relative plasmon intensities by nonlinear effect on matrix optical constants. At $R \geq 20$ nm there are higher-order modes in a spectrum.

An extinction spectrum of a bimetallic particle transforms between that for a homogeneous sphere made of a shell material and that for such sphere made of a core material, whereas p ranges from 0 to 1. At intermediate p a spectrum depends in a complicated manner both on core and shell permittivities relation and on particle and core radii.

The obtained regularities can be used to control optical characteristics of nonlinear systems based on metal coated nanoparticles as well as for optical diagnostic of interior structure of small metalline double-layer particles.

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P4.6

RAMAN SPECTROSCOPIC STUDY OF NANOCRYSTALLINE SEMICONDUCTING METAL SELENIDE THIN FILMS

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Raman spectra of several nanocrystalline semiconducting metal selenide thin films (Ag_2Se, HgSe, CuSe, Cu_3Se_2), as well as of the thin films of elemental (amorphous and metallic) selenium, and of the corresponding bulk materials were recorded.

The investigated thin solid films were obtained by chemical bath deposition tecnique, employing the hydrolitic decomposition of sodium selenosulfate. The crystalline size of the specimen was varied controlling the deposition conditions (*pH*, temperature) as well as by post-deposition annealing.

All of the studied nanocrystalline materials exhibit size quantization effects, evident from both the appearance of the UV/VIS spectra and the calculated band gap energies (in comparison to the bulk values). The Raman shifts corresponding to the LO modes of the investigated thin films and the corresponding bulk materials were measured, and an evidence for the appearance of lower-frequency bands corresponding to the surface phonon (SP) modes in the nanocrystalline structures is presented. The variation of Raman shifts, widths and intensities of the bands corresponding to LO and SP modes with the crystalline size was followed, employing methods of band-shape analysis.

The obtained results are consistent with the assignment of the bands in question as due to the surface phonon modes in the quantum-confined nanostructures.

STRUCTURAL AND OPTICAL PROPERTIES OF NANOSTRUCTURATED TITANIUM OXIDE LAYERS

P4.7

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The nanoporous nanocrystalline TiO_2 layers appear to have significant technological potential and, in the last period, have been the subject of increased scientific interest. The potential applications that have been reported include dye-sensitized regenerative photo-electrochemical cells [1], lithium-insertion batteries, electrochromic windows [2], and just electroluminescent devices [3]. Progress in performance of titanium oxide within these applications could be achieved by specific structural control over the characteristics of the material. This control is possible based on the processing details by which chemical reactivity is related to nucleation and growth of titania.

This paper presents the results of our efforts in direction of optimizing and standardizing the processing conditions for anatase titanium oxide obtained as nanoporous nanocrystalline (nanostructurated) layers deposited on crystalline silicon substrate. The control and monitoring over structure and organization of TiO_2 nanocrystals has been achieved by means of wet chemistry. The oxide clusters and nanocrystallites have been synthesized in aqueous solution by hydrolysis and polycondensation of several titanium alkoxides in the presence of a basic medium. The TiO_2 layer samples were performed by depositing freshly prepared solutions on (100) silicon wafer.

The titanium oxide layers were investigated using two different spectroscopic techniques: spectroscopic ellipsometry (SE) and infrared (IR) spectroscopy. SE was used to determine the microstructure details of TiO_2 layers (composition, thickness, and porosity) and the influence of processing parameters: stoichiometry of the reactions (precursor combination ratio), autoclaving temperature and pressure, rate of evaporation of the solvent, stirring. The titania layers were simulated by Bruggemann theoretical model (Effective Medium Approximation - EMA) [4] considering a mixture of TiO_2 and voids. Measurements were done in the spectral range of 1.77 - 3.1 eV. These parameters are presented and discussed here. The features of IR spectra have been used to extract information concerning stoichiometry (oxygen content), bond strain and density (porosity) and to identify impurities incorporated in the films. Correlations between the data obtained from the two spectral methods have been accomplished.

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P4.8

STUDY OF PHTHALOCYANINES FOR APPLICATION IN SOLAR ENERGY CONVERSION

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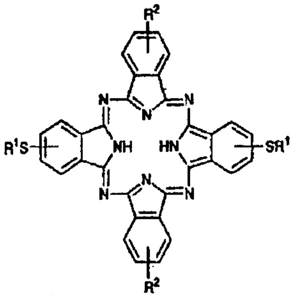
Phthalocyanines are synthetic dyes which can be used as photosynthetizers in solar energy conversion devices [1]. In our previous papers [2,3] we have investigated porphyrin dyes and their substituted and metallic complexed derivatives solved in nematic liquid crystal. In this contribution we have studied spectroscopic and photoelectric properties of two sulphonated phthalocyanines (Pc) shown in Fig. 1.



	R^1	R^2
Pc 55	$CH_2CH_2N^+Me_3$-$CH_3SO_4^-$	NO_2
Pc 56	$CH_2CH_2N^+Me_3$-$CH_3SO_4^-$	NH_2

Fig. 1. Chemical structure of investigated phthalocyanines

Dyes were dissolved in polyvinyl alcohol with dimethylsulfoxide. The pathways of deactivation of dyes excited states were examined by absorption, fluorescence and photoacoustic spectroscopy. Spectroscopy parameters were determined. The competition among radiative, non-radiative and charge separation processes in Pc 55 and Pc 56 is discussed. The later process determines the process of photocurrent generation. Photocurrent kinetics and photovoltaic action spectra for Pc 55 and Pc 56 in photoelectrochemical cell constructed of semiconducting and metallic electrodes have been measured.

The differences in Pc 55 and Pc 56 molecular structure are expected to influence their effectiveness in photocurrent generation. The ability of Pc 55 and Pc 56 photocurrent generation has been shown. Thus we have shown that this dyes can be used in solar energy conversion devices. The comparison of data presented in this paper for Pc 55 and Pc 56 and for porphyrins [2,3] has been discussed.

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CHARACTERIZATION OF ULTRA-THIN POLYMER FILMS BY POLARIZATION MODULATION FTIR SPECTROSCOPY

P4.9

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Ultra-thin polymer films play a crucial role in modern micro- or nanosystems. Established techniques to form such films are the self assembly (SA) technique or the Langmuir Blodgett (LB) technique. Especially in case of new materials, the necessary quality of the ultra-thin films - highly ordered and homogeneous molecule arrangements - is not always achieved. Polarization modulated (PM) FTIR spectroscopy is particularly suited to reveal the degree of orientational order/disorder of molecules bound to the dielectric or metallic surfaces, because only molecular vibrations with distinctly oriented dipoles are excited. Here we report on the results for SA and LB layers on different substrates.

Our PM equipment is based on a FTIR spectrometer (IFS 88, Bruker Optik GmbH, Ettlingen, Germany) equipped with a MCT detector. Light from the interferometer is polarized linearly by a wire-grid polarizer and subsequently modulated by an optical active ZnSe crystal (PEM-90, HINDS Instruments, Hillsboro, Oregon, USA). The reflection unit (Graceby Specac, Fairfax/VA, USA) allows either external and internal reflection measurements. All components fit into the sample chamber of the spectrometer and can be purged completely with dry air. This ensures a high energy throughput and a good S/N ration even in regions of high isotropic atmospheric absorption.

SA layers of bis-(11,11'-carboxy-undecyl)-disulfide ($[COOH\text{-}(CH_2)_{11}\text{-}S]_2$) on gold and of 17-Cyanoheptadecyl-trichlorosilane ($CN\text{-}(CH_2)_{17}\text{-}Si\text{-}Cl_3$) on silica were formed by adsorption from solution. An external reflection arrangement was used for these investigations.

The disulfide spectra show only weak vibrational bands of the methylene and carbonyl groups. The weak absorption reveals a severe disorder among adsorbed molecules. In contrast to spontaneously adsorbed SA layers, spectra taken under identical conditions from LB mono- and bilayers of the same sulfide show stronger absorption bands, which indicates a higher degree of molecular orientation obtained by the LB technique. In addition, progression bands could be observed in this case. The spectra of the trichlorosilane mainly exhibit a vibrational band of carbonyl groups. As the appearance of this band indicates, upon adsorption the molecules are subject to a chemical reaction from nitrile via amid to carbonic acid. This reaction is caused by the high local concentration of HCl upon covalent binding of the trichlorosilane to the silica substrate. Despite this reaction the molecules are arranged in a highly ordered state.

P4.10

EVIDENCING PHASE SEPARATION IN POLYMER BLENDS BY MEANS OF PHOTO - AND ELECTROLUMINESCENCE STUDIES

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Electroluminescent polymers are attracting much attention not only due to the fundamental interest in the study of processes related to their charge- and photoexcitations, but also due to their potential application in opto-electronic devices, such as light-emitting diodes (LEDs). The use of polymer blends is a commonly used strategy to improve the efficiency of polymer-based LEDs, since they ideally allow the separation and control of charge transport and luminescence efficiency. In this communication we report on the use of polyfluorene-based blends in single- and double layer LEDs. From the electroluminescence spectra of double-layer LEDs, we obtained first evidence for phase separation upon contact of a thin film of the blends with acetone, which is a non-solvent. This observation was further confirmed by photoluminescence investigations of the blends upon contact with other non-solvents at room temperature. Quite interestingly, Atomic Force Microscopy (AFM) was not sensitive enough to provide conclusive evidence for such phase separation process. Photo- and electroluminescence, when appropriate, appear therefore as very sensitive techniques to probe phase separation in polymer blends.

VIBRATIONAL SPECTRA AND DFT CALCULATIONS OF PPV-OLIGOMERS

P4.11

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Poly(*p*-phenylenevinylenes) (PPVs) are known as potential materials for application in electroluminiscence devices. The first three members of the PPV-oligomer family were synthesized and their infrared and Raman spectra recorded. These are: 1,4-distyrylbenzene (DSB), *p, p*'-distirylstilbene (DSS) and (1,4-distyryl-4,4"-distyryl)benzene (DDB). The structure of the compounds is not known due to their very poor solubility (for NMR measurements) and nonavailability of single crystals (for X-ray analysis).

Molecular geometries were optimized by the HF method with the 6-31G* basis set, giving symmetries belonging to point groups C_s, C_2 and C_1 respectively. Calculations of vibrational spectra, including IR intensities were carried out using the DFT method (6-31G* basis set). Vibrational wavenumbers, potential energy distributions and IR intensities are in a fair agreement with our own experimental spectra. The results are compared with the very elaborate calculation of the vibrational spectrum of *trans*-stilbene (tSB). Whereas in tSB the olefinic C=C stretching is strongly coupled with the C-H in-plane deformation, in the three PPV-oligomers a trend is pronounced towards a "pure" C=C stretching mode.

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P4.12

OPTICAL PROPERTIES OF Mn^{3+} IONS IN Cs_2NaAlF_6 AND Cs_2NaGaF_6 SINGLE CRYSTALS

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Recent advances in tunable solid-state lasers have generated a strong interest in developing and investigating new compounds that emit in the visible and near-infrared spectral regions [1-5]. Common to all these materials is the use of 3*d* transition metal ions as active ions. The unfilled 3*d* electronic shell of these ions has a number of low-lying energy levels, between which the optical transitions can occur and generate the luminescent emission. As the 3*d* electrons are on the outside of the ions, the optical spectroscopic properties of the metal transition ions are directly affected by the static and dynamic properties of their environments. Then, the optical associated spectra are characterized by both sharp and broad bands. These broad bands are due to the strong electron-phonon coupling. Moreover, many studies in the scientific literature have shown that the Jahn-Teller effect can strongly influence the optical spectra of the Mn^{3+} ion in octahedral coordination [6-8]. This effect distorts the ^5E ground state and augments the complexity of the observed structures in the optical spectra. In this work, the optical properties of Mn^{3+} ions in the hexagonal elpasolites Cs_2NaAlF_6 and Cs_2NaGaF_6 have been investigated by emission, excitation and absorption spectroscopies at different temperatures. Each compound has two crystallographically inequivalent octahedral sites for the Al^{3+} and Ga^{3+} ions that can be occupied by Mn^{3+} ions [9]. The observed transitions in the spectra are assigned and the crystal field parameter *Dq* and the Jahn-Teller stabilization energy are determined.

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UV-VIS DIFFUSE REFLECTANCE SPECTROSCOPIC STUDY OF TRANSITION-METAL (V, Ti) CONTAINING CATALYSTS

P4.13

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Transition metal ions (especially V^{4+}, Ti^{4+}) isomorphously substituted into the tetrahedral framework of molecular sieves have been considered as promising catalysts for selective oxidations. The activity and selectivity of these catalysts were found to be sensitive to the nature of V and Ti species in the silicate matrix. Their oxidation state, coordination sphere and topology influence the catalytic activity and selectivity [1].

Incorporating transition metal ions may be performed via isomorphous substitution during synthesis or by post-synthetic techniques like traditional or solid-state ion exchange. The reflection mode of UV-vis spectroscopy proved to be a powerful method for characterizing these materials, the oxidation state of the transition metal ions and the influence of pretreatment, such as burning the template off after synthesis.

A Perkin-Elmer Lambda 15 spectrometer equipped with a reflectance accessory and a home-made sample holder containing 0.2 g solid powder was applied. MgO was used as reference in the measurements.

The spectra of air-calcined V-MCM-41 proved the presence of V^{5+} in tetrahedral coordination. After exposure to wet air a new band developed near 440 nm indicating the presence of some vanadium in distorted octahedral-coordination. From this follows that the stability of V^{5+}-ions in framework position, i.e. in tetrahedral coordination is low. A part of these ions releasing the framework occupy extraframework positions.

A novel template removal method was applied rendering burning at relatively low temperature (150 °C) [2]. O_3 was used instead of air to compare the influence of calcination temperature which is generally 550 °C. The advantages of previous method were supported by the spectra of Ti-MCM-41. The difference in spectra obtained for air and ozone calcined Ti-MCM-41 helps to understand the nature of catalytically active titanium species. Our results support Ti in tetrahedral position to be the catalitically active centres.

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P4.14

RAMAN STUDIES OF COMPOSITION AND THERMAL TREATMENT EFFECTS ON THE STRUCTURE OF SOL-GEL DERIVED GeO_2-SiO_2 THIN-FILMS

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Germano-silicate glasses with controllable indices from 1.46 to 1.6, are used for their compatibility with optical fibres. But they are also important because of their photosensitive properties, i.e. their refractive indices can be permanently modified by laser irradiation. This last property is the basis of the inscription of Bragg gratings, essential for the conception of optical integrated devices.

The object of the present work is to use Raman spectroscopy to investigate first, the structural changes due to variations in the germanium content of sol-gel derived germano-silicate materials and secondly, to monitor modifications due to thermal treatment. The glasses were prepared in the form of ultra-thin optical-quality films because the waveguide configuration is important for integrated optics.

A study of Waveguide Raman WRS spectra shows that characteristic bands in the Raman spectrum of pure silica assigned to ring defects are absent for the germano-silicate systems, thus indicating the destabilizing effect of the inclusion of GeO_2 in the matrix. Changes in position and profile of bands assigned to νTOT (T= Si or Ge), νSi-O-Ge and νGe-OH, as well as to the boson peak are correlated with structural variations evolving in the network. The average TOT angle, for example, increases with annealing temperature. This last observation suggests that the germanosilicate network evolves towards a system in which the average size of the polyhedral rings increases.

Low-frequency Raman studies of the boson-peak region show that the position of the boson peak evolves towards high frequencies with annealing temperature. Moreover, an increase in germanium content leads also to an increase in the peak frequency. These observations are indicative of a decrease in the diameter of cohesive domains within the glassy structure and consequently of an increase in the degree of the densification process.

FT RAMAN SPECTROSCOPY AS A TOOL TO CHARACTERIZE NOVEL SORBENTS BASED ON DERIVATIZED SILICA GEL

P4.15

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Vibrational spectroscopic techniques have been recently used as diagnostic tool to verify derivatization of chromatographic substrates. The possibilities of infrared spectroscopy are rather limited because silica gel is opaque in quite broad range; Raman spectra of derivatized materials are more accessible [1]. The problems of intense fluorescence and of the weakness of Raman scattering have to be solved.

This study is focused on verification of individual steps of synthesis of new sorbents based on derivatized aminopropylated silica gels [2]. Two different optically active compounds were used for preparation of stationary phases: (+)-CLOPROSTENOL [CAS RN 54276-21-0] (Fig. 1), and (R)-(+)-1,1'-binaphtol-3-carboxylic acid (Fig. 2).

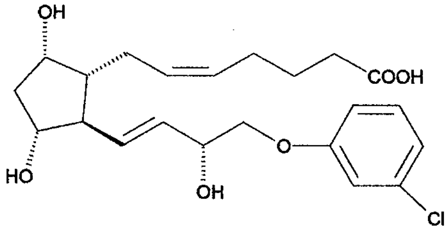

Fig. 1 - (+)-CLOPROSTENOL

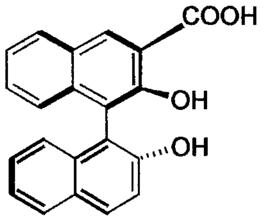

Fig. 2 - (R)-(+)-1,1'-binaphtol-3-carboxylic acid

Firstly, FT Raman spectra of pure compounds and of aminopropylated silica gels were obtained. Then the chiral derivatization agents (Fig. 1, 2) were connected to propyl chains by amide bonds. Finally, free silanol groups were covered by trimethylsilyl groups. Both synthetic steps were verified by FT Raman spectroscopy. The results of the study enable not only qualitative verification of synthetic steps, but also a semi-quantitative determination of covering of the sorbent surface by derivatization agent. The quantitative methods are developed on the basis of comparison of spectral data with the data obtained from elemental analysis.

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P4.16

RAMAN SPECTROSCOPIC CHARACTERISATION OF ER^{3+} - DOPED OXIDE TELLURITE GLASSES

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The synthesis of a novel class of glasses for the conception of optical-fiber amplifiers is of great importance for optical industries and in glass science, in general. Tellurite glasses are of much interst because they possess a relatively broad transmission region (0.35 - 5 µm), good thermal stability, large refractive indices and high dielectric constants.

Erbium-doped tellurites were prepared from TeO_2, PbO, ZnO, Er_2O_3 and Na_2O crystalline powders. These powders were placed in alumina crucibles and melted in a tubular furnace. The addition of sodium oxide served to increase the rare-earth solubility.

Raman spectroscopic investigations were undertaken to study the influence of the presence of the erbium dopant as well as of the concentration of Na_2O. For the systems $(1\text{-}x\text{-}y)TeO_2$ - x PbO - y Er_2O_3, it was found that the introduction of even small amounts of Er^{3+} ($y < 0.1\%$) results in a decrease in intensity of the TeO_4 band, thus indicating that the ions facilitate the conversion of TeO_4 units into TeO_{3+1} and /or TeO_3 groups. However, when the concentration of erbium is greater than 1%, the opposite effect occurs. Indeed, it appears that the oxygen atoms of erbium oxide serve to repair the polyhedral chain, and TeO_3 groups are transformed into TeO_4 units. Because the erbium ions are very large, they prevent the PbO units from intercalating in the chain (in the case of high concentrations of PbO). This interpretation is supported by the reappearance of the band at 450 cm^{-1} for this sample, a band which is assigned to bending modes of PbO groups. In the case of the systems $(1\text{-}x\text{-}y)TeO_2$ - x ZnO - y Er_2O_3, the effects are similar but much weaker.

TRI-L-VALINE SELENATE – STUDY OF VIBRATIONAL SPECTRA AND STRUCTURAL PHASE TRANSITION

P4.17

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The addition compounds of amino acids with inorganic oxyacids are a part of our research project focused on study of hydrogen bonded solids potentially exhibiting ferroelectric properties or proton conductivity. Tri-L-valine selenate (TVSe) and di-L-valinium selenate monohydrate [1] are two compounds found in L-valine – selenic acid – water system.

FTIR and FT Raman spectra of natural and deuterated TVSe were measured and interpreted. The results obtained lead to the conclusion that crystal structure of the compound is formed by selenate anions (SeO_4^{2-}), L-valinium cations ($(CH_3)_2CHNH_3^+CHCOOH$) and L-valine zwitterions ($(CH_3)_2CHNH_3^+CHCOO^-$) (in the ratio of 1:2:1) interconnected by a system of hydrogen bonds. According to position of ν O-H and ν N-H vibrational bands in infrared spectra the length and symmetry of O-H...O and N-H...O hydrogen bonds are discussed.

The natural and deuterated TVSe were further studied by the DSC (temperature range 95-333 K) and low temperature FTIR spectroscopy (temperature range 90-298 K). Mechanism of the first order type low temperature structural phase transition found at 138 K is discussed.

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P4.18

FTIR AND FT RAMAN STUDY OF L-LEUCINE - SELENIC ACID ADDITION COMPOUND

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Di-L-leucinium selenate (DLSe), the only compound found in L-leucine – H_2SeO_4 - H_2O system, is a new member of the family of aminoacid addition compounds which are undoubtedly a structurally interesting and technically important substances.

Polycrystalline samples of DLSe were examined by FTIR and FT Raman spectroscopy and obtained spectra were interpreted also for partially deuterated compound. The findings of this study enable to define that crystals of DLSe are formed by L-leucinium cations ($(CH_3)_2CHCH_2NH_3^+CHCOOH$) and selenate anions (in the ratio of 2:1) which are connected by an extensive system of hydrogen bonds. On the basis of correlation curves [1, 2] the length of these bonds was estimated from the positions of their vibrational manifestations in the spectra.

"Positive isotopic effect" [1] on deuteration is discussed and deductions concerning the potential energy curve of the short H-bonds are presented.

FTIR measurements (down to 90 K) and DSC measurements in a broad temperature interval were carried out to elucidate the existence of possible phase transitions.

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NMR STUDY OF THE NEW CHIRAL CALIX[4]ARENES

P4.19

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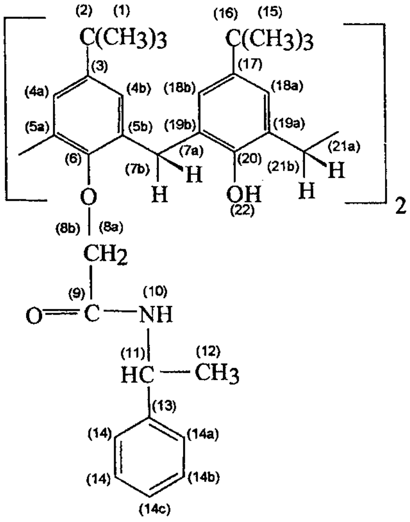
Recently the synthesis of several new diester and tetraamide based on calix[4]arene skeleton have been reported[1,2]. In this communication new chiral ligands **1** and **2** were studied by means of one- and two- dimensional homo- and heteronuclear experiments (NOE-diff, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC and HMBC) at 500,13 MHz. These experiments allowed to assign also both signals of noneqvivalent protons 7(a), 7(b), 8(a), 8(b) and signals of carbons 4(a), 4(b), 5(a), 5(b) of ligand **1** which are resolved in ^{1}H, resp. ^{13}C NMR spectrum. Our results show that the conformation of **1** in solution is very similar to the conformation in solid state (X-ray crystallography)[2].



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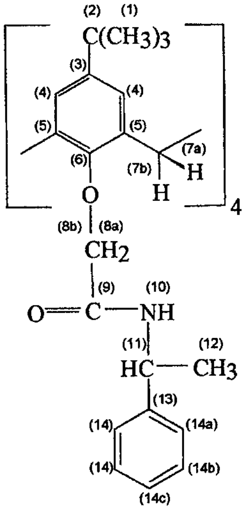

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P4.20

SPECTRAL AND THEORETICAL STUDY OF SOME NEW 4-STYRYL COUMARINE DERIVATIVES IN ALCOHOL SOLUTIONS

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The use of 4-styryl-coumarines as pH-sensors is based on the quino-imidic [1] structures of these compounds in wich - OH group stabilization has an important role.

Four new 4-styryl coumarine recently prepared were studied from the point of view of their pH-sensor quality. NMR, IR spectra, electronic absorption and emission spectra in non-polar and in alcohols were studied.

Changes in the band intensities have been evidenced in the fluorescence electronic spectra and in IR spectra depending on the pka of the alcohols.

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THEORETICAL AND EXPERIMENTAL ELECTRO-OPTICAL STUDIES OF SOME NEW PYRIDAZINIUM YLIDES

P4.21

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Some new carbanion mono- and di- substituted pyridazinium ylides were spectrally analyzed by NMR, FTIR, UV.VIS, and DRS means.

Quantum mechanical computation evidenced a delocalization of the negative charge on the carbanion substituents and the high reactivity as nucleophylic reagents in organic syntheses of pyridazinium ylides.

In alcohols, a color decreasing in time was evidenced, emphasizing a hydrogen intermolecular bond formation between the ylidic carbanion and hydroxyl group of alcohol. The kinetics of this reaction has been studied, from the optical density decreasing in the visible absorption spectra.

The solvent influence on the electronic absorption visible band has been also studied.

The electric dipole moments of the analyzed molecules have been estimated both from the solvent influence on the visible intramolecular band of the ylides and by the dielectric constant measurements at infinite dilution. Quanto-mechanical values were in a good agreement with those experimentally obtained.

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P4.22

ON THEORETICAL VCD, IR AND RAMAN SPECTRA OF MODEL CHIRAL TREFOIL KNOTS

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Recently, we have studied the stability of various model topological carbyne $(C°C-)_{2n}$ isomers: knots, links, and cyclized hook and ladder structures [1-6]. We have shown that the knot stability, measured through the knot-cycle energy difference, decreases with the number of C-atoms in the knotted carbyne molecule, and that the energy difference increases in line with the knot type series from 0_1 to 6_3. We have also reported on the symmetry of some of the C_{2n} knotted carbynes and on the resulting theoretical NMR [1-4] and IR [1] spectra showing how such topological isomers can be experimentally identified.

We have reported also on the structure and energetics of two-component carbyne links - C_{60} catenated carbynes [5] and C_{60} carbyne cyclized hook and ladder structures [6]. In particular, we have demonstrated the energy changes to accompany changes the cycles size in the series $(C_{60-2n}C_{2n})$, where $20\ ^3\ n\ ^3\ 5$. Such a relationship can exhibit from one to several minima depending in the number of crossings and the topological type. This means that, for the link and cyclized hook and ladder molecules with several crossings, some isomers can be obtained much easier than the others.

Some knots and links are chiral due to sheer topology rather than geometry. In the present paper we show an analysis of the theoretical (HF/3-21G) vibrational circular dichroism, IR, and Raman spectra of two trefoil 3_1 carbyne knots that have the same D_3 symmetry but different size: C_{30} and C_{60}. We analyzed the C°C stretching vibration region only (30 and 15 vibrations for C_{60} and C_{30} knots, respectively) and show that theoretical VCD spectra exhibit clearly knots chirality. The discussion of the spectra is supported by PED analysis.

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Solid State Spectroscopy

-Crystals
-Amorphous Solids

AB INITIO HF SCF AND FOURIER TRANSFORM INFRARED STUDY OF THE STRUCTURE, VIBRATIONAL FORCE FIELD AND CHARGE DISTRIBUTION IN TWO *o*-SUBSTITUTED *S*-PHENYL THIOBENZOATES

P5.1

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Continuing our studies of *o*-substituted *S*-phenyl thiobenzoates [1-4], we present a combined experimental and theoretical study of two members of the mentioned series: *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate. Room and low-temperature solid-state Fourier-transform infrared spectra of the mentioned compounds were recorded and tentative empirical assignment of the most important bands was proposed. In fact, these compounds have already been studied by spectroscopic methods, but only in solutions.

In order to get a deeper insight into the spectroscopic properties of these species, as well as a more solid basis for band assignments, a computational study was also performed. The geometries of the two molecules were optimized at the Hartree-Fock SCF level of theory, using Berny's optimization algorithm (computing the energy derivatives analytically). The standard double-zeta quality 3-21G(d,p) basis set was used for orbital expansion. Numerical harmonic vibrational analyses were performed for the optimized geometries, in order to test their character and to obtain the harmonic vibrational force field. The computed structural parameters were compared to those obtained crystallographically [4]. The obtained scaled harmonic vibrational frequencies are in a very good agreement with the experimental ones, confirming the applicability of HF/3-21G(d,p) scaled harmonic force field for a study of species with more than 12 atoms.

The charge distribution within the *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate was studied using several charge – assignment schemes, on the basis of the computed HF/3-21G(d,p) wavefunctions corresponding to the optimized geometries. These included the Mulliken algorithm, the natural population analysis, as well as the electrostatic potential based schemes such as CHelp, CHelpG and MK.

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P5.2

RAMAN SPECTRA OF SOME SALTS OF PYROMELLITIC ACID CONTAINING HYDROGEN BONDS

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Experimental and theoretical studies have demonstrated the dependence of intensity and frequency of hydrogen bond vibrations on its strength[1]. Carboxylic acids and carboxylate ions have been a inexhaustible source of hydrogen bonds.

In this work the Raman spectra were recorded for three salts: 1- hexaaquairon(II) dihydrogen-1,2,4,5-benzenetetracarboxylate [$FeC_{10}H_4O_8.6H_2O$]; 2- triaquacopper(II) dihydrogen-1,2,4,5-benzenetetracarboxylate trihydrate [$CuC_{10}H_4O_8.6H_2O$]; 3-triaquacopper (II) 1,2,4,5-benzenetetracarboxylate tetrahydrate [$Cu_2C_{10}H_2O_8.10H_2O$].

The crystal structure of the compounds are known and they crystallize in the monoclinic system. The Fe salts is a ionic compound and the iron atom was coordinated to six water molecules. In the compounds 2 and 3 the copper atoms are coordinated to three water molecules and two carboxyl groups of two pyromellitate ions forming a polymeric structure. The separation (Δ) between symmetric and asymmetric carboxylate stretching vibrations can be used as a parameter to identify the coordination type[2]. In Fe salt the value of Δ is 141 cm^{-1} and in copper salts it is about 343 cm^{-1}. These results are in agreement with the crystallographic structures.

The Fe salt has a short intramolecular hydrogen bond with a $O\cdots O$ distance of 2.381Å. In the compound 2 was observed two medium intermolecular hydrogen bonds (2.638Å and 2.627Å) and compound 3 does not have hydroxyl group so the pyromellitate ion is a receptor to medium hydrogen bonds with water molecules.

The short hydrogen bond stretching observed in the Raman spectra was assigned to a broad band of weak intensity in 874 cm^{-1} for asymmetric mode [$\nu_{asym}(O\cdot\cdot H\cdot\cdot O)$] and in 307 cm^{-1} for the symmetric [$\nu_{syn}(O\cdot\cdot H\cdot\cdot O)$] one. These modes had been observed in other salts to pyromellitic acid which have short intramolecular hydrogen bond[3]. Since these regions have many modes, the attributions of stretching to hydrogen bonds was done to deconvolution methods and confirmed by *ab initio* calculations for the pyromellitate ion. On the other hand in copper salts similar bands were not observed in these regions. The $\nu(O\cdot\cdot H\cdot\cdot O)$ of long and medium hydrogen bond is expected in low frequencies (about 120 cm^{-1}). However this region has lattices and hydrogen bonds water modes which makes difficult the attribution of $O\cdot\cdot H\cdot\cdot O$ mode.

In spite of the fact that the $O\cdot\cdot H\cdot\cdot O$ mode lies in crowed region of the spectrum, it was possible to identify and attributed these stretching. Information about different types of hydrogen bond (short or long) can be obtained using Raman spectroscopy.

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RAMAN SPECTROSCOPY OF BALL MILLED TiO_2

P5.3

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The Raman spectroscopy is method to analyze different crystal structure of TiO_2. We applied it in order to study structural changes during high-energy ball milling of TiO_2 powder. TiO_2 anatase (tetragonal structure, space group $I4/amd \equiv D_{4h}^{19}$) was milled up to 10 hours using two different sets of vials and balls. The first set was made of wolfram carbide (WC) and the other of agate. In addition to structural changes, ball milling caused decrease of TiO_2 particles to nanometric size. As a novel approach the low-frequency Raman spectroscopy was used for monitoring of diminution of the TiO_2 particle and determination of nano sizes. The most intensive band of TiO_2 anatase was shifted to higher frequency as an evidence of nanosized particles.

The kinetics of milling and sequence of resulting structures depend on milling set. After five minutes of milling of anatase structure in WC set the new bands were detected in Raman spectrum. They were assigned as band of high-pressure TiO_2(II) phase (α-PbO_2 structure, space group $Pbcn \equiv D_{2h}^{14}$). However, three hours of milling in WC set was needed for transformation from high-pressure phase to rutil (tetragonal structure, space group $P4_2/mnm \equiv D_{4h}^{14}$). When milling was performed by agate set the anatase structure was transformed directly to rutil structure of TiO_2. Raman spectra showed that transformation to rutil started after approximately 30 minutes of milling with agate set and it was completed after 10 hours of milling. Different behavior due to the different milling set was the consequence of different mass of balls, and therefore the different energy was transferred to TiO_2 powder.

Based on long time theoretical result of Lamb[1], it was known that diameter of the particle is inverse proportional to the frequency of the lowest-energy spherical mode of a free particle corresponding to angular momentum $l=0$. In our work, the low-frequency Raman band was broad with maximum appeared in range from 10 to 30 cm^{-1} depending on milling time and milling set used. The broadness suggests the wide dispersion in nano-particle dimensions, while position of low-frequency band point at dimensions from 7 to 21 nano meters.

Raman spectroscopy enabled us to monitor structural and dimensional changes caused by high-energy ball milling.

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P5.4

RAMAN SPECTRA OF METAL(II) 4-METHYLBENZENESULFONATE SALTS (METAL(II)∈{Cu, Co, Ni, Pb}) . A COMBINED GRADIENT-CORRECTED DENSITY FUNCTIONAL AND EXPERIMENTAL STUDY

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Raman spectra of the series of metal(II) 4-methylbenzenesulfonate salts (where metal(II)∈{Cu, Co, Ni, Pb}) were recorded. The bands were empirically assigned and a comparative analysis with the corresponding benzenesulfonate salts was carried out.

In order to get a more exact basis for the band assignments, a density functional study of the 4-methylbenzenesulfonate anion was performed. The geometry of the anion was fully optimised at gradient-corrected DFT level of theory, with Berny's optimization algorithm (computing the energy derivatives with respect to nuclear coordinates analytically). Becke's three-parameter hybrid exchange functional was used in combination with the Lee-Yang-Parr correlation one (B3-LYP). The standard double-zeta quality 6-31+G(d,p) basis set, supplemented with diffuse functions for a better description of the anionic wavefunction was used for orbital expansion to solve the Kohn-Sham equations.

Subsequent numerical harmonic vibrational analysis was performed in order to test the character of the stationary point found on anionic potential energy hypersurface, and to obtain the harmonic vibrational frequencies. Raman intensities were calculated using the perturbational finite-field methodology. The internal torsional motion was studied basing on the DFT energetics of various possible conformers. The torsional energy levels were calculated within the internal rigid rotor approximation, diagonalising the torsional Hamiltonian within the free rotor basis.

The gradient-corrected DFT methodology further confirmed our recently proposed reassignments of several bands in the IR and Raman spectra of compounds containing 4-methylbenzenesulfonate and benzenesulfonate anions.

QUANTUM CHEMICAL STUDY OF THE WATER BENDING POTENTIAL IN COMPOUNDS OF THE MKPO$_4$·H$_2$O TYPE

P5.5

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The water bending potential in crystalline compounds of the $MKPO_4 \cdot H_2O$ type (where M∈{Mg, Ni, Co, Mn}) which exhibit *very large* red shift of the δ(HOH) frequency was studied by quantum chemical methods.

In order to get a deeper quantitative insight into the factors influencing the large shifts of the δ(HOH) frequency in the studied systems, a quantum chemical study of the "free-molecule" and the "in-crystal" δ(HOH) potential was carried out within the finite cluster approach. The finite clusters consisted of a water molecule and its nearest neighbours within the crystallographic unit cell [1], treated both explicitly and as point charges. The vibrational potential energy curves for the (uncoupled) HOH bending vibrations were obtained from pointwise energy calculations at Hartree-Fock SCF level of theory (all other structural parameters of the cluster were held fixed at the experimental values for the "in-crystal" calculations). The obtained energies were least-squares fitted to a fourth order polynomial in $\Delta\alpha = \alpha_{HOH} - \alpha_{HOH,e}$ (where $\alpha_{HOH,e}$ is the equilibrium value of the H–O–H angle) with a model function of the form:

$$V = V_0 + \tfrac{1}{2} k_{\alpha\alpha} r_{OH,e}^2 (\Delta\alpha)^2 + k_{\alpha\alpha\alpha} r_{OH,e}^3 (\Delta\alpha)^3 + k_{\alpha\alpha\alpha\alpha} r_{OH,e}^4 (\Delta\alpha)^4$$

($r_{OH,e}$ is the equilibrium value for the O–H distance), and the one-dimensional vibrational Schrödinger equation was solved variationally, diagonalizing the vibrational Hamiltonian within the harmonic oscillator basis. For the pointwise energy calculations at the HF SCF level of theory, two basis sets were used for orbital expansion. The first of these is the standard LANL2DZ basis which includes an effective core potential (ECP) description of the inner shell electrons (D95V on the first row elements, and Los Alamos ECP plus DZ on the others). The other one consisted of the standard triple-zeta quality 6-311++G(3df,3pd) basis on H, P and O, and LANL2DZ on M and K. From the calculated energies of the vibrational eigenstates, both the fundamental *anharmonic* and harmonic δ(HOH) vibrational frequencies, as well as the anharmonicity constants were computed. According to the quantum chemical results, the overall red shift of the fundamental δ(HOH) frequency in the studied systems may be attributed mainly to the variations in the harmonic force constant ("flattening of the potential").

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P5.6

STUDY OF LATTICE DYNAMICS IN δ-KH(IO$_3$)$_2$ CRYSTAL BY INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION

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Ionic-covalent crystals from the family of acid iodates of the general formula mM(IO$_3$)·nH(IO$_3$), (M-metal or ammonium cation, n, m = 1, 2 ...) are known to possess intriguing physical properties such as high values of electric permittivity or proton conductivity, non-linear optic and dielectric characteristics etc. Such features are attributed to peculiar behavior of iodine atoms in the crystal lattice, namely to their ability to expand its trigonal pyramidal coordination sphere, which results in dynamical lattice disorder. It this paper we deal with potassium biiodate stable modification δ-KIO$_3$·HIO$_3$ which is of special interest because of low temperature phase transition, non-linear dielectric and optical properties, and a suggested dynamic jump type proton disorder. Crystal structure of the crystal has been recently re-examined [1]. It was shown that at room temperature δ-KH(IO$_3$)$_2$ crystal structure (F*dd*2, Z=24) consists of $[I_3O_9H_{3/2}]^{3/2-}$ ions possibly originating from occupationally disordered $[I_3O_9H_2]^-$ and $[I_3O_9H]^{2-}$ anions. These ions are connected via hydrogen bonds to form plane grids parallel to (100) direction with the K^+ ions placed between them. Some peculiarities of the lattice dynamics have been observed by IR and Raman spectroscopy which could not be explained in the frame of solid-solid phase transitions. The peculiarities manifest themselves in distinct temperature evolution of IR absorption bands related to the in-plane bending vibration δ(OH) of I-O-H···O-I fragments at about 220 K [1].

In this paper we apply temperature dependent FTIR spectroscopy to obtain detailed information about proton dynamics in δ-KH(IO3)2 crystal in the temperature range from 13 to 300. The fine structure of ν(OH) stretching vibration band (2700 cm-1) observed below 220 K seems to indicate the significant coupling between low-frequency and high-frequency H-bond vibrations. As it follows from our powder X-ray diffraction studies, there is no structural changes in anionic lattice in the temperature range from 90 to 295 K. Thus the continuous changes in intermode coupling constants with temperature, which reflect the changes in dynamic state of protons, are more probable to be responsible for observed spectral features. The comparison of experimental spectra with their computer simulation by means of strong coupling oscillators model [2] allowed to obtain fitting parameters which appeared to be in good agreement with the expected values.

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FOURIER TRANSFORM INFRARED SPECTRA OF DITTMARITE

P5.7

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The Fourier transform infrared spectra of dittmarite ($MgNH_4PO_4 \cdot H_2O$) and a series of its deuterated analogues were recorded at room temperature (RT) and at the boiling temperature of liguid nitrogen (LNT).

Dittmarite is biomineral which is found quite infrequently in urinary calculi [1]. It can be obtained by dehidration of struvite.

In the RT and LNT infrared spectra of dittmarite, several bands between 3600 and 2500 cm^{-1} are found. The spectral picture in this region is very similar to that found in the case of the corresponding hexahydrate (struvite) which suggests the existence of strong hydrogen bonds in the present case as well. The analysis of the spectra of dittmarite and its deuterated analogues indicates that the two highest frequency bands at 3429 and 3400 cm^{-1} are due to the antisymmetric and symmetric stretching vibrations of water molecules with C_{2v}, C_2 or C_s symmetry.

In the spectra of the slightly deuterated analogue (≈ 3 % D), three prominent bands (at ≈ 1316, 1300 and 1283 cm^{-1}) appear in the region of ND bending vibrations of isotopically isolated NH_3D^+ ions,. Their frequency is very high for this kind of vibrations [2], which again suggests the presence of very strongly hydrogen bonded ammonium ions (in accordance with the picture in the ND stretching region).

The triply degenerate ν_3 and ν_4 modes (the notation is that for free phosphate ions) are active in the infrared. Unlike the spectrum of struvite were only one band is found in the region of the ν_3 and ν_4 modes, several bands appear in this region of the spectrum of dittmarite which implies a lower symmetry of the phosphate anions in the studied compound.

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P5.8

VIBRATIONAL SPECTRA OF CADMIUM CHLORIDE MONOHYDRATE

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The Fourier transform infrared spectra of cadmium chloride monohydrate and a series of deuterated analogues were recorded at room temperature (RT) and at boiling temperature of liquid nitrogen (LNT). The Raman spectrum of the protiated compound was also recorded.

The monohydrate of cadmium chloride crystallizes in the orthorombic system (space group P_{nma} with $Z = 4$) [1]. The crystal structure consists of $[CdCl_4(H_2O)Cl]$ octahedra packed along [010] and linked by hydrogen bonds. Water molecules of a single type (situated on mirror planes) form two different hydrogen bonds of the O · · · Cl type.

The appearance of a single H–O–H bending band (at 1589 cm^{-1}) in the RT infrared and Raman spectra of the protiated compound is in accordance with the existence of one crystallographic type of water molecules. Identical frequencies in both types of spectra are indicative of absence of a correlation-field splitting. The frequency of this band (lower then the corresponding one in gaseous water) should be pointed out. The appearance of two bands (at 2584 and 2574 cm^{-1}) due to uncoupled O–D stretching modes agrees with the existence of nonequivalent hydrogen bonds. The small frequency difference between these two bands indicates that the force field for the stretching O–D vibrations is almost identical. The OD stretching region of the spectra of the partially deuterated analogues also support such a conclusion.

In the region of water libration only one strong band (at around 560 cm^{-1}) is observed in the infrared spectra, whereas no band is found in this region of the Raman spectrum.

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VIBRATIONAL SPECTRA OF HEXAAQUA COMPLEXES. X. RAMAN AND IR STUDIES OF THE SULFATE GROUP DISORDER IN α-ALUMS

P5.9

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Both X-ray diffraction and Raman spectroscopic studies [1,2] indicated that the sulfate groups in some aluminium α-alums are orientationally disordered. The current studies of the Raman and IR spectra of various alums give evidence that the disorder is indeed present in a number of sulfate α-alums. This is best manifested through the appearance of surplus bands in the spectral regions of the symmetric (Raman) and antisymmetric (IR) stretching vibrations of the sulfate anion. The extent of disorder was reconfirmed to be cation-sensitive, the smaller the univalent cation, the larger the disorder. The spectroscopic results are in an excellent agreement with the crystallographic ones. A sulfate group disorder was also detected in sulfate-doped selenate alums. However, no spectroscopic evidence was found for selenate group disorder, again in agreement with the crystallographic results for pure selenate alums.

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P5.10

CONVENTIONAL AND DIFFUSE REFLECTANCE FOURIER TRANSFORM INFRARED SPECTRA OF THE DIAMMINESILVER PENTACYANONITROSYLFERRATE(II) COMPLEX

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The conventional Fourier transform infrared (FTIR) spectra of the $[Ag(NH_3)_2][Fe(CN)_5NO]$ complex were recorded, as KBr pellets, at room temperature (RT) and the boiling temperature of liquid nitrogen (LNT).

The band due to the NO stretching mode is single at both RT and LNT, whereas the corresponding CN band is, in line with the expectations, split. The self-deconvolution of this band did not reveal any new features. As in the case of $[Ni(bpy)_3][Fe(CN)_5NO] \cdot 4H_2O$, the lowering of the temperature leads to blue shifts of the $\nu(CN)$ and $\nu(NO)$ bands.

Also affected by the temperature change are the bands due to NH_3 stretchings but in this case the temperature coefficient $d\nu/dT$ is *positive.* At LNT the broad $\nu(NH_3)$ feature is split into at least two components.

The bands in the N–H/N–D stretching regions are not well resolved even at low temperatures. In the spectrum of the slightly deuterated compound, the bands in the N–D stretching region are centered slightly above 2500 cm^{-1} which is indicative of not very strong hydrogen bonding (the gas-phase value for the ν_3 mode of NH_2D is 2484 cm^{-1}).

The conventional FTIR spectra were compared with the diffuse-reflectance (DR) FTIR spectra.

FOURIER TRANSFORM INFRARED SPECTRA OF TRIS(BIPYRIDINE)NICKEL(II) PENTACYANONITROSYLFERRATE(II) TETRAHYDRATE AND OF ITS PARTIALLY DEUTERATED ANALOGUES

P5.11

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The Fourier transform infrared (FT IR) spectra of the title compound, $[Ni(bpy)_3][Fe(CN)_5NO]\cdot 4H_2O$ and of its partially deuterated analogues were recorded at room temperature (RT) and the boiling temperature of liquid nitrogen (LNT). The recorded spectra are similar to those of the analogous tri(bipyridine)iron(II) complex.

In the region of water stretchings a complex and temperature-sensitive feature is observed with several rather clearly defined submaxima on it. In the O–D stretching region of the spectrum of the analogue containing a small amount of deuterium, at least seven components are observed in the self-deconvoluted LNT spectra. This, of course, is a clear indication that several (very likely – four) crystallographically different types of water molecules exist in the structure.

The broad and temperature-sensitive bands found below 750 cm^{-1} are easily attributed to water librations.

Even at RT, the CN and NO stretching bands are split, the splitting being more pronounced at LNT. On going from RT to LNT interesting blue shifts are observed for both ν(CN) and ν(NO), the shift being larger in the latter case.

P5.12

FOURIER TRANSFORM INFRARED SPECTRA OF STRUVITE

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The infrared spectra of magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$ (often referred to by its mineralogical name struvite) and of its partially deuterated analogues were recorded from room temperature (RT) down to the boiling temperature of liquid nitrogen (LNT).

Struvite is a well-known biomineral and its major biological importance is related to its presence in human urinary sediments and vesical and renal calculi [1].

The crystal structure of $MgNH_4PO_4 \cdot 6H_2O$ was solved by neutron diffraction [2]. According to the crystallographic results, it crystallizes in the orthorhombic space group $Pmn2_1$ with $Z = 2$. It was found that Mg^{2+}, PO_4^{3-} and two (out of four) types of water molecules occupy special positions with C_s symmetry, while the other two types lay on general positions. The crystallographic data do not suggest disorder in the ammonium group. The water molecules donate some of the shortest hydrogen bonds ever found in crystalline hydrates [3].

The existence of strong hydrogen bonds between water molecules is supported by the appearance of a broad band from 3800 to 2200 cm^{-1} in the stretching region of the infrared spectrum. In the region of the $\nu_4(NH_4)$ modes, more than two strong bands are found in the RT spectrum, whereas in the LNT spectrum only two bands can be seen. In the RT spectrum of the analogue with a small deuterium content (≈ 2 % D), in the region of the ND bending vibrations of isotopically isolated NH_3D^+ ions, two bands (at around 1290 cm^{-1} and 1250 cm^{-1}) are observed whereas four bands can be seen in the corresponding LNT spectrum. All this implies the existence of some kind of disorder of the ammonium ion, at least at subambient temperatures.

In the region of $\nu_3(PO_4)$ modes one strong and broad band is found, while in the region of the $\nu_4(PO_4)$ bending vibration and of the external modes of the water molecules, several bands can be seen. On the basis of a careful analysis of the RT and LNT spectra of the protiated compound, as well as those of its partially deuterated analogues, we assigned the band at 574 cm^{-1} to the $\nu_4(PO_4)$ modes and the remaining ones as due to librational and translational modes of the water molecules.

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VIBRATIONAL STUDIES OF THE SOLID IMIDAZOLE AND PYRIDINE ADDUCTS OF METAL(II) SACCHARINATES.

P5.13

III. Zn(II) AND Hg(II) IMIDAZOLE SACCHARINATES*

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As a part of the continuing structural study of the metal saccharinates, two novel imidazole adducts of Zn(II) and Hg(II) saccharinates were prepared. In order to elucidate some structural characteristics of these compounds, the regions of the OH/OD, NH/ND, CO and SO_2 vibrations in their FT IR spectra recorded at room and at liquid-nitrogen boiling temperature were investigated.

The infrared spectra of the studied complexes are different from each other and also different from those of the imidazole saccharinates of Co(II), Ni(II) [1], Mn(II), Fe(II) [2], Cu(II) [3] and Cd(II) [4]. Neither of the studied compounds, therefore, is a member of the series of isomorphous imidazole saccharinates $[M(Im)_4(H_2O)_2](sac)_2$ (M = Mn, Fe, Co, Ni; Im = imidazole; sac = saccharinato ion).

Similarly to the other known Hg(II) saccharinates, the imidazole adduct of Hg(II) saccharinate is anhydrous, supported by the absence of water vibrational bands in the corresponding spectrum. The spectroscopic data reveal eventual presence of two structurally different imidazole molecules with very weakly hydrogen bonded imino groups in its structure. A single type of C_{2v} water molecules is supposed for the structure of the Zn(II) complex.

Only one ν(CO) band was assigned in the spectrum of Hg(II) imidazole saccharinate, while at least two ν(CO) bands are candidates for such assignment in the case of the Zn(II) complex. From the frequency difference of the assigned carbonyl stretching bands in the spectra of the studied complexes it can be concluded that the metal–saccharinato bonding in the Hg(II) complex, similarly to Hg(II) 2,2'-bipyridine saccharinate, is mostly ionic, while the character of the corresponding bonding in the Zn(II) compound is between typically covalent and ionic. The spectroscopic data for the SO_2 stretchings in the infrared spectrum of Zn(II) imidazole saccharinate support the presumptions about the presence of more than one crystallographic types of saccharinato ligands in the respective structure.

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* For part II of this series see Reference 2.

P5.14

SPECTRA–STRUCTURE CORRELATIONS IN SOLID METAL SACCHARINATES. I. THE CARBONYL STRETCHINGS

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Analysis of the results from a literature survey of carbonyl stretching modes in the infrared spectra of solid metal saccharinates is presented. Data for more than 90 assigned ν(CO) bands in the IR spectra of nearly 55 solid saccharinates, molecular saccharin and the saccharinato nitranion (the latter as a diluted DMSO solution), including the results from the authors' own work, are considered. An attempt was made to derive empirical equations which would correlate the observed ν(CO) frequencies with the structural characteristics of the respective carbonyl groups, such as the determined C–O distances or the C–O bond orders calculated using various BDBO (bond order–bond length) schemes [1]. The relevant structural data were mainly extracted from the recent survey of saccharinato structures in the Cambridge Structural Database [2].

The results have shown that, although in certain cases this may be so, in general the raw ν(CO) frequencies of the solid saccharinates can not be used for very accurate quantitative prediction of the structural parameters of the carbonyl groups. Presumably this is a result of the influence of various solid state factors on the appearance of the ν(CO) spectral region. Additional structural factors, such as eventual coordination or hydrogen bond formation through the carbonyl oxygen, may also contribute to the poor predictive power of the ν(CO) modes. Aside of this and along with some earlier observations [3], the ν(CO) frequency or its shift from the corresponding infrared value of pure saccharin indeed *can* be used as a qualitative criterion for estimation of the degree of covalency of the metal–N(saccharinato) bonding. Three exceptional cases that comprise neutral saccharin molecules in the respective structures and higher ν(CO) frequencies than the frequency of saccharin were found: M(Hsac)(sac)$\cdot$$H_2O$ (M = Rb, Cs [4]) and [VO(OH)(sac)(Hsac)$(H_2O)_2$] [5]. The lowest-frequency ν(CO) modes were observed in a series of rare earth metal saccharinato salts [6].

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VIBRATIONAL STUDIES OF THE SOLID IMIDAZOLE AND PYRIDINE ADDUCTS OF METAL(II) SACCHARINATES.

P5.15

II. Mn(II) AND Fe(II) IMIDAZOLE SACCHARINATES*

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Within an ongoing systematic structural study of the metal saccharinato salts and complexes and their adducts with *N*-donor bases, novel imidazole adducts of Mn(II) and Fe(II) saccharinates were synthesized and the FT IR spectra of their protiated and partially deuterated analogues were recorded at room and at liquid nitrogen boiling temperature. The characteristic spectroscopic data concerning the OH, OD, NH, CO and SO_2 groups were used together with the earlier spectra-structure correlations to make structural presumptions about the complexes.

The infrared spectra of the Fe(II) and Mn(II) imidazole saccharinates show close resemblance with those of the ismorphous Co and Ni compounds of formula $[M(H_2O)_2(Him)_4](sac)_2$ (Him = imidazole, sac = saccharinato ion) [1] and probably feature similar structures with the latter. Similarly to what was found in the case of the Co and Ni imidazole saccharinates, the integrated intensities of the two isotopically isolated ν(OD) bands are unexpectedly different, the higher-frequency one being more prominent. The appearance of the ν(OD) spectrum, analogously to the Co and Ni complexes, indicates existence of a single crystallographic type of asymmetrical water molecules in their structures. Several empirical ν(OD) frequency–*d*(O···A) (A = acceptor) relations were used to predict the O···A distances.

A single band in the spectra of the studied compounds was prescribed to the carbonyl stretching mode. The value of the frequency shifts of the carbonyl stretching modes from the ν(CO) mode of molecular saccharin reveals that the metal–saccharinato bonds are predominantly ionic. The assignment of a single pair of sulfonyl stretching bands in their spectra, on the other hand, is an indication that all saccharinato ions are structurally equal.

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* Part I of the series is the Reference 1.

P5.16

MINERALS FROM MACEDONIA. V. FT IR STUDY OF GYPSUM, BARITE AND THEIR SYNTHETIC ANALOGUES

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The most frequently used complementary techniques for mineral characterization are X-ray diffraction (e.g., ref. 1), Raman (see, e.g., [2]) and infrared vibrational spectroscopy [3]. Continuing our study of the structural and spectroscopic characteristics of the minerals originating from Macedonia, we studied the FT IR spectra and the X-ray diffraction patterns of some carbonate minerals [4–6] and reported some preliminary results for gypsum and barite [7].

Here we present the results of the study of the FT IR spectra of gypsum ($CaSO_4 \cdot 2H_2O$) and barite ($BaSO_4$) from various localities in Macedonia (Debar, Delcevo and Probištip for gypsum and Zletovo and Dobrevo for barite). Contrary to the predictions, it was found that the band originating from the ν_2 mode (expected at around 450 cm^{-1}) does not appear in the infrared spectra of gypsum and barite. This was interpreted as being due to the high *effective* symmetry of the force field for this mode. On the other hand, it was shown that the spectra of the natural minerals differ from those of their synthetic analogues, the differences being especially pronounced in the region of the ν_3 sulfate modes. Also studied was the spectrum of the mineral which was previously characterized as anhydrite. Although, compared to gypsum, its morphological characteristics (shape, color and transparency) are quite different, it was shown that the studied mineral is in fact gypsum.

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MINERALS FROM MACEDONIA. IV. DISCRIMINATION AMONG SOME CARBONATE MINERALS BY FT IR SPECTROSCOPY

P5.17

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Various techniques and procedures for mineral detection, identification, discrimination and for their quantitative determination have been developed during the last few decades. The most frequently used among them are X-ray diffraction, thermal analysis, optical diffuse reflectance, Raman and infrared vibrational spectroscopy. Since all these techniques have their own advantages and shortcomings, it is strongly recommendable (especially in the case of mineral characterization) to use them in a complementary, rather than competitive, manner.

Very often, however, it is advantageous to use (or to develop) rapid and simple methods for mineral discrimination as well as for detection of impurities in mineral mixtures using *only one* of the above mentioned techniques, e.g., X-ray powder diffraction or Fourier transform infrared spectroscopy. Both techniques, namely, yield results quickly and provide a rapid indication about the presence of impurities. As a part of a broader study of the structural and spectroscopic characteristics of minerals originating from Macedonia, we have previously studied the analytical application of FT IR spectra and X-ray diffraction patterns in the case of the carbonate minerals calcite and aragonite [1–3] while presently we describe the use of FT IR spectroscopy to distinguish among these two and some other geologically important carbonate minerals (siderite, magnesite and dolomite) and detect mineral impurities in them, as well as to compare the spectra of the natural minerals and their synthetic analogues. In the course of the quantitative determination of the composition of mixtures it was shown that the limit of detection of impurities is around 2 %.

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P5.18

SPECTRAL CHARACTERISTICS OF *O*-PHENANTROLINE SACCHARINATO COMPLEXES WITH COBALT(II), NICKEL(II), ZINC(II) AND MANGANESE(II). COMPARISON WITH THE CORRESPONDING 2,2′-BIPYRIDINE SACCHARINATES

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The RT and LNT infrared spectra of protiated and partially deuterated analogues of the title compounds in the HOH, HOD, CO and SO_2 stretching region were studied. Their spectral characteristics were compared with the structural data for $Mn(phen)_2(sac)(H_2O)]^+sac^-$ (phen denotes *o*-phenantroline, sac stands for saccharinato ligands) [1,2].

Since the *o*-phenantroline and 2,2′-bipyridine ligands are similar, the spectral characteristics of the title compounds were compared with the spectral [3] and structural [4] characteristics of the corresponding 2,2'-bipyridine compounds, as well, It was found that, contrary to the isomorphous series of the metal 2,2′-bipyridine saccharinato complexes of Co(II), Ni(II), Zn(II) and Mn(II), only the phenantroline saccharinato complexes of Co(II) and Ni(II) are, most probably, isomorphous, while Mn(II) and Zn(II) complex exhibits some spectral differences which are most pronounced in the HOH stretching region. These differences are related to the geometry of the water molecule. Other parts of the spectra are similar to each other.

The comparison of the infrared spectra of metal phenantroline saccharinates (metal = cobalt, nickel) with the spectra of the corresponding metal 2,2′-bipyridine saccharinates refers to possible structural similarity between them. In spite of that, some differences were observed in the stretching SO_2 region. The pronounced split of the bands due to the $\nu(SO)_2$ modes in the spectra of metal phenantroline saccharinates was, namely, observed. It was taken as an indication that the SO_2 angle in the structure of the title compounds is larger than the found average value for all metal saccharinates.

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INFRARED STUDY OF THE VERY LOW WATER BENDING FREQUENCIES IN COMPOUNDS OF THE $MKPO_4·H_2O$ TYPE

P5.19

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Fourier transform infrared (FT IR) spectra of the compounds of the $MKPO_4·H_2O$ type (where M∈{Mg, Co, Mn}) and of their deuterated analogues were recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT). All of the studied systems exhibit *very large* red shift of the δ(HOH) frequency compared to almost all other systems studied so far.

In the FT IR spectra of the protiated magnesium compound, no band of significant intensity is found in the region above 1600 cm^{-1} where bands due to the δ(HOH) mode(s) are expected to appear. On the contrary, a band of appreciable intensity appears about 100 cm^{-1} *lower* than the gas-phase value. The origin of this band as due to the δ(HOH) mode was confirmed by the spectra of partially deuterated analogues. The situation in this case is quite similar to that encountered with $NiKPO_4·H_2O$ [1].

However, in the case of $MnKPO_4·H_2O$, two bands of almost equal intensities appear both above and below 1600 cm^{-1} whereas the situation with $CoKPO_4·H_2O$ is intermediate between that of $MgKPO_4·H_2O$ and $MnKPO_4·H_2O$.

The anharmonicity of δ(HOH) modes in the studied series of compounds was studied as well by analizing the overtone spectral region.

On the basis of the known crystal structure of one of the members of the series ($MgKPO_4·H_2O$), a tentative model is proposed, based on the Lennard-Jones type potential, which explains the frequency *lowering* of the δ(HOH) modes in these crystalline hydrates.

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P5.20

INFRARED AND RAMAN SPECTRA OF SELENATE IONS ISOMORPHOUSLY ISOLATED IN POTASSIUM, RUBIDIUM AND CESIUM SULFATES. LATENT SYMMETRY *VS.* FERMI-LIKE RESONANCE EFFECTS

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Room and low-temperature (~ 100 K) Fourier transform infrared and room temperature Raman spectra of $M_2Se_xS_{1-x}O_4$ solid solutions (where $M \in \{K, Rb, Cs\}$, while $x = 0.02$ and 0.05) were recorded. Special emphasise was put on the region of appearance of bands due to the impurity (selenate) anions.

The appearance of the spectra of dopant species is generally consistent with a C_s site-symmetry of the isomorphously isolated SeO_4^{2-} anions. However, noticeable differences from the analogous $M_2Se_{1-x}S_xO_4$ solid solutions are evident. Thus, the splitting between the medium and the lowest-frequency component of the $\nu_3(SeO_4)$ mode (the antisymmetric stretching) is significantly smaller than the splitting between the highest-frequency and the medium component, leading to a spectral appearance which is somewhat *between* the C_s and C_3-effective symmetry. Although such findings are usually rationalised in terms of the so-called *latent symmetry* effects, in the present work we present an alternative explanation of the observed phenomenon. Since the lowest-frequency component of the ν_3 mode of the dopant SeO_4^{2-} anions is nearly-degenerate with the corresponding ν_1 mode (the symmetric Se-O stretch), the spectral picture may be explained in terms of a Fermi-like resonance. This phenomenon was treated in a deeper and more quantitative way. Expressions were derived on the basis of the stationary perturbation theory for the degenerate case, which allows a *quantitative* prediction of the importance of these Fermi-like resonance effects *vs.* the latent symmetry effects. The proposed model is easily applicable to other similar systems as well.

The anharmonicity of the stretching vibrations of dopant species within the studied series of matrices was studied as well, on the basis of the regions of the second-order vibrational transitions involving these modes. Conclusions regarding the distortion of the SeO_4^{2-} anion in the isomorphous potassium, rubidium and cesium sulfate matrices were derived on the basis of the observed vibrational Stark splittings of the ν_3 and ν_4 mode components.

EXPERIMENTAL AND CALCULATED SPECTRA ^{1}H, ^{13}C AND ^{15}N NMR OF FAMOTIDINE AND ITS METALLOCOMPLEXES WITH NI(II)

P5.21

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Famotidine[1,2] (Fig.1), 3-[[[2-[(aminoiminomethyl)amino]-4-thiazolyl]methyl] thio]-N-(aminosulfonyl), is a histamine H_2-receptor antagonist, used for treatment of peptic ulcers and Zollinger-Ellison syndrome and is a very effective ligand for metal ions. Interpretation of experimental NMR spectra of famotidine was compared with quantum chemical calculation based on methods: B3LYP/6-31G* for geometry optimization and Hartree-Fock/6-31G* for magnetic properties of the drug.

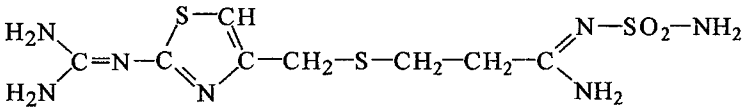

Fig.1-Famotidine

In this work we present spectroscopic characterization of two solid state nickel(II)-famotidine complexes. The coordination of Ni^{2+} begins at pH above 5 and the monodentate coordination of thiazole nitrogen was suggested. The increase of pH, above 7.5, causes change of the octahedral geometry of famotidine-Ni(II) complex into square-planar one with simultaneously release of two protons.

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P5.22

RAMAN STUDIES OF FERROELASTIC $[(CH_3CH_2)_3NH]SbCl_6$

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$[(CH_3CH_2)_3NH]SbCl_6$ (TEACA) belongs to a family of the alkylammonium halogenoantimonates(V). Up to now five salts from this family have been studied: $[P(CH_3)_4SbCl_6$ [1], $[C(NH_2)_3]SbCl_6$ [2], $[N(CH_3)_4]SbCl_6$, $[N(C_2H_5)_4]SbCl_6$ [3] and $(C_5H_{10}NH_2)SbCl_6{*}(C_5H_{10}NH_2)Cl$ [4]. Some of these salts exhibit ferroelastic properties in ordered low temperature phases.

The x-ray, differential scanning calorimetry, linear thermal expansion, dielectric measurements and Raman spectra are used to investigate the properties of TEACA crystal. It has been found that the title salt undergoes first order structural phase transition at 336 K. The changes of thermodynamic parameters indicate an order-disorder character of this transition. The shape of dielectric anomaly at 336 K indicates the rotational character of the transition.The TEAAC reveled a ferroelastic domain structure at room temperature.

The Raman spectra of the powdered sample in the wavenumber region of 3350 - 50 cm^{-1} were carried out in the temperature range 300 - 355 K. The distinct changes of the position and bandwidth of a band assigned to the stretching NH vibration as well as of bands assigned to the anionic internal vibrations are observed. Unexpectedly very weak changes in the Raman spectra of TEAAC around the phase transition point are found for the C-C and C-N stretching vibrations. Such changes are usually observed if we deal with limitation of freedom of rotation of triethylammonium cations on cooling. One can conclude that both the dynamic of cationic and anionic sublattices contribute to the mechanism of the phase transition at 336 K.

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MnO_4^- AND MnO_4^{2-} MOLECULAR CENTERS IN CUBIC LATTICE: NEAR INFRARED LUMINESCENCE AND RESONANCE RAMAN SPECTRA

P5.23

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We report on the first observation of the near-infrared luminescence in RbI crystals doped with the MnO_4^{2-} (manganate) and MnO_4^- (permanganate) ions.

In MnO_4^{2-} doped crystals a broad-band emission spectrum extends from 8500 cm^{-1} to 11000 cm^{-1}. The temperature dependence of the luminescence has been studied at temperatures from 300 K to 4 K. The electron-phonon structure of the luminescence spectrum was observed at low temperatures at Ar^+ laser excitation by pumping ^2E-$^2T_2$ ($1t_1$-$2e$) optical absorption band of the MnO_4^{2-} ion. The optical absorption in visible region is due to an intramolecular ligand-to-metal charge-transfer process from the oxygen atoms to the manganese ion. The NIR-luminescence is attributed to the d-d ($^2T_2$ - ^2E) transitions of the single d- electron of the MnO_4^{2-} ion.

Luminescence in the near infrared spectral region similar to that for MnO_4^{2-} doped iodides was observed in MnO_4^- doped RbI and KI crystals. Permanganate ions were obtained by coloration of the $RbI:MnO_4^{2-}$ and $KI:MnO_4^{2-}$ crystals. The NIR luminescence was also excited in the visible region via $^1A_1$-$^1T_2$ ($1t_1$-$2e$) charge transfer process intra MnO_4^- ion.

At 4 K the luminescence spectrum displays a well-resolved vibronic structure in both matrices. The vibronic structure observed can be considered as a result of E x e Jahn-Teller coupling in the ground electronic state. The intensity measurements of MnO_4^- induced luminescence show that with decreasing temperature the intensity at first grows up to about 104 K. However, below this temperature the decay of the spectrum is registrated. To clarify the nature of this effect we studied the resonance Raman spectra of MnO_4^- doped iodide crystals at 5145 Å excitation. The photoinduced decrease of the NIR luminescence intensity is correlated with corresponding intensity bleaching of Raman intensity observed at low temperatures. To explain the origin of the luminescence in the case of permanganate ion (Mn^{7+}) we consider a transient Mn^{6+} state of the permanganate ion generated in the charge transfer process.

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P5.24

SPECTROSCOPIC EVIDENCES OF JAHN-TELLER PHASE TRANSITION IN THE MIXED $CsDy_{1-x}Bi_x(MoO_4)_2$ CRYSTALS

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Layered rhombic double molybdates of the family $M^IM^{III}(MoO_4)_2$ reveal the sequences of phase transitions of different types which take place in the temperature region from 300K down to helium temperatures. The aim of this work is to investigate the phase diagram of caesium-dysprosium and caesium-bismuth double molybdates and mixed $CsDy_{1-x}Bi_x$ crystals (x = 0.1, 0.2, 0.3, 0.5, 0.7). We study the low-temperature Jahn-Teller phase transition which takes place in $CsDy(MoO_4)_2$ at 42K and the influences of Bi doping on this feature. The polarised far-infrared spectra (20 – 500 cm^{-1}), polarised reflectance spectra (400 – 1000 cm^{-1}), absorption spectra (3100 – 40000 cm^{-1}), temperature dependence of birefringence and visual observations of the domain structure at phase transition have been measured. Hysteresis loops at the phase transition of the first order type were obtained too. The dependence between the composition and the internal and external vibrational modes was studied for the mixed compounds. The results were discussed in terms of the simplified one-dimensional model of layered crystals.

FTIR STUDIES OF MIDDLE RANGE ORDER IN THE CYCLOSILICATE-LIKE STRUCTURES

P5.25

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In silicate structures, the ring system indicates the existence of middle range order. The FTIR spectra in the range of pseudolattice vibrations can be a very useful tool for recognizing this type order. The isolated rings also occur in other structures described as cyclosilicate-like ones. In the present paper infrared investigations of cycloaluminosilicates, cycloaluminates and cyclogermanates were carried out. By means of factor group analysis it has been shown that only one intensive band, characteristic of ring structures should be observed on IR spectra of cyclosilicates. The ring band position is related to the number of ring members [1]. It has been pointed out that infrared studies can be useful for ring identification in nonsilicate structures. The studies of (MgO-Al_2O_3-SiO_2, SrO-SiO_2 SrO-GeO_2, BaO-GeO_2) systems allowed to show the influence of different ring cations (Si^{+4}, Al^{+3}, Ge^{+4}) on the ring band positions. The presence of aluminium cations, lighter than silicon cations, causes the shift of ring band to higher wavenumbers. In the case of cyclogermanates, as there is the big mass difference between germanium and silicon, the ring band is observed in the significant lower wavenumber range. The examinations of cyclogermanates with different non-ring cations such as Sr^{+2} and Ba^{+2} can show the influence of these cations on the position of the bands.

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P5.26

SPECTROSCOPIC STUDIES OF THE $NaCaPO_4$-$AlPO_4$-SiO_2 SYSTEM

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Some phosphosilicate materials can be used as biomaterials; they should contain SiO_2 for good mechanical and chemical properties and CaO for biological compatibility. The influence of the presence of Al_2O_3 on properties of such materials is very interesting. In the $NaCaPO_4$-$AlPO_4$-SiO_2 system aluminium should not be harmful for tissue because of high stability of Al-O-P bonds in $AlPO_4$ complex. On the other hand it should be advantageous from the point of view of the material structure. The change of materials structure which can interpret their properties can be estimated on the base of vibrational spectroscopy studies.

A series of materials containing 80 mole% of SiO_2 and 0-20 mole% of $AlPO_4$ and $NaCaPO_4$ respectively was prepared using pseudo aqua solutions of aerosil or sol-gel method. IR spectra of the obtained materials were measured in different temperatures using both transmission and diffuse reflectance spectroscopy technique. In the high temperature spectra (temperature about 500 K) we can observe polymorphous transition between low and high temperature of cristobalite-like structure phases. Low temperature spectra (liquid helium temperature) can help to find the bands connected with lattice vibrations.

It has been found that the interpretation of spectra of multicomponent $NaCaPO_4$-$AlPO_4$-SiO_2materials enables to connect the spectra form with the samples composition.

Mixing the $AlPO_4$-SiO_2 and the $NaCaPO_4$-SiO_2 systems mak chance to obtain homogenous materials promising for bioceramics. The addition of Al_2O_3 should not be a source of soluble aluminium but should improve homogeneity of these materials.

BRILLOUIN-SCATTERING STUDY OF $KAl(MoO_4)_2$ AND $NaAl(MoO_4)_2$

P5.27

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The polarized Brillouin spectra have been measured at 293 K for trigonal $KAl(MoO_4)_2$ and monoclinic $NaAl(MoO_4)_2$ crystals. These crystals belong to the large family of layered double molybdates and tungstates in which transitions to ferroelastic phases have been found. The phase transitions occur between the D_{3d}^3 structure and the C_{2h}^6, C_{2h}^3 or C_i structures. $KAl(MoO_4)_2$ crystal may be regarded as a model crystal for the paraelastic D_{3d}^3 phase. From the other side, $NaAl(MoO_4)_2$ crystal is a good candidate for a model crystal of the ferroelastic C_{2h}^3 structure since it may be easily obtained in a monodomain form. The observed differences in the Brillouin spectra, recorded for the both crystals, are discussed in terms of the differences in the crystal structures. The measured frequencies of acoustic modes propagating perpendicular to the layers are used to provide information on the origin of some IR active lattice modes.

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P5.28

SPECTRAL AND THEORETICAL STUDIES ON THE MOLECULAR AND CRYSTALLINE STRUCTURE OF SOME 2-(2'PYRIDYL)-PYRIDINIUM YLIDES

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To establish their molecular geometry and the crystalline structure, some new, highly stabilized cycloimmonium ylides derivatives of bipyridyl [1,2] have been studied by means of FTIR, UV-VIS and ^{1}NMR spectra.

The charges on the atoms, the bond lengths and their spatial orientation have been estimated by quantum mechanical, ab initio and semiempirical calculations.

Evidenced by ^{1}NMR and theoretical means, the intramolecular hydrogen bond between the carbanion substitutes induces a great stability of these compounds.

X-Ray diffraction permited us to describe the molecular and crystalline structure of the studied 2-(2'-pyridyl)-pyridinium carbanion disubstituted ylides.

The experimental data are in good agreement with the theoretical ones.

Quantum mechanical calculation emphasized the reactivity as nucleophylic reageants in organic synthesis of 2-(2'-pyridyl)-pyridinium carbanion disubstituted ylides.

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IR AND ESR STUDIES ON SOME DIMERIC COPPER(II) COMPLEXES

P5.29

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The copper(II) p-clorbenzoates $[Cu_2R_4 \cdot CH_3OH \cdot 2H_2O]$ (I) and $[Cu_2R_4 \cdot CH_3COCH_3 \cdot 2H_2O]$ (II), where R = $(p\text{-}ClC_6H_4CO_2)$ dimeric complexes (Fig.1) as well as their monomeric species which occur at 77 K have been investigated using IR and ESR spectroscopy.

The coordination of the copper(II) ions at the carboxylat –COO group arises from the appearance of the stretching vibration ν(Cu–O) at 475 cm^{-1} and the combination frequencies $\nu(Cu\text{–}O)+\delta_{ring}=690$ cm^{-1}, $\nu(Cu\text{–}O)+\delta(O\text{–}C\text{=}O)=770\div800$ cm^{-1} in the IR spectra of studied complexes. Both compounds present two water-type molecules, some involved in hydrogen bonds (ν_{as}(H–OH)=3400 cm^{-1}) and the other chlatrate molecules (ν_{as}(OH)=3585, 3609 cm^{-1}). By heating the two complexes at 110 °C, the broad band at 3400 cm^{-1} disappears, while the hydroxyl stretching bands dissapears only at 170° owing to the strong bonding between the water and complexes molecules. The comparison between the adsorbed water in the unheated complexes was estimated from the ratio between the intensity of the stretching (at 3400 cm^{-1}) and bending (at 1600 cm^{-1}) water vibrations. This ratio is 0.070 for the complex (I) and 0.112 for the complex (II) which indicate a greater amount of water for the complex (II). The temperature dependance of the IR spectra also shows that the complex (II) loses more water like complex (I).

The room temperature powder ESR spectra of the axial copper(II) p-clorbenzoates complexes are typical for randomly oriented triplet state species (S=1) with a short Cu-Cu distance (≈2.64 Å) [1]. The 77 K spectra indicate the coexistence of monomeric and dimeric species. The appearance of monomeric species at low temperatures can be attributed to the water molecules contained in matrices of the studied complexes. By freezing these lead to an increase of the Cu-Cu distance and thus to the breaking of the spin-spin coupling with their rearrangement in monomeric forms. The complex (I) presents two monomeric species, one with square-planar local symmetry D_{4h} ($g_{\parallel} = 2.301$, $g_{\perp} = 2.067$, $A_{\parallel} = 174 \cdot 10^{-4}$ cm^{-1}, $A_{\perp} = 21.4 \cdot 10^{-4}$ cm^{-1}) and the other with octahedral symmetry given by the coordination of two water molecules along the Oz axis ($g_{\parallel} = 2.327$, $g_{\perp} = 2.046$, $A_{\parallel} = 174 \cdot 10^{-4}$ cm^{-1}, $A_{\perp} = 21.4 \cdot 10^{-4}$ cm^{-1}). The complex (II) has only the octahedral species ($g_{\parallel} = 2.324$, $g_{\perp} = 2.044$, $A_{\parallel} = 165 \cdot 10^{-4}$ cm^{-1}, $A_{\perp} = 43 \cdot 10^{-4}$ cm^{-1}).

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P5.30

VIBRATIONAL SPECTRA OF AUGELITES $Al_2(OH)_3(XO_4)$ (X = P, As, V)

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The crystal structure of natural augelite $Al_2(OH)_3(PO_4)$ (**1**) was determined some time ago ($C2/m$, $Z = 4$) [1]. It contains aluminium in octahedral and trigonal-bipyramidal coordinations with two different μ_2- and μ_3-OH groups bridging the two different aluminium atoms. There are no appropriate O···O distances for hydrogen bonds with these OH groups as donors. Recently, the structure of synthetic augelite-d_3 was refined and the D nuclei were located by neutron diffraction [2]. Also, an iso-morphous vanadate and arsenate $Al_2(OH)_3(XO_4)$ (X= V, As) were prepared and structurally studied [3,2].

A unit-cell group analysis was performed. As a result the vibrations of the primitive unit-cell ($Z' = 2$) classify into the symmetry species of $C_{2h} - 2/m$ as:

$$\Gamma_{vib} = 22\ A_g + 17\ B_g + 15\ A_u + 21\ B_u$$

In addition a detailed classification of both valence and deformation modes was per-formed combining different approaches.

The predicted three ν(OH/D) modes are clearly observed in the IR spectra of As-augelite and As-augelite-d_3 as high-frequency narrow bands; in augelite only two sharp ν(OH) absorptions (3550, 3475/2627,2579 cm^{-1}) appear. These findings pre-clude hydrogen bonds (see above). The expected δ- and γ-modes of the Al_2OH or Al_3OH fragments are partly obscured by the completely split $\nu(XO_4)$ and $\delta(XO_4)$ vibra-tions in the optical spectra, but they dominate the inelastic neutron scattering (INS) spectra. Thus, the strongest band in the INS spectrum of **1** at 1010 cm^{-1} (strong in IR 1025 cm^{-1}, shift on deuteration to 803 cm^{-1}, Raman 1047 cm^{-1}) is to be assigned to the δ-modes preferably in the Al_2OH fragments. The δ-modes in the Al_3OH groups and/or γ-modes appear as strong INS features and in IR spectra (900/825 cm^{-1} and 922/844 cm^{-1}, respectively). The frequency ranges 750 to 400 cm^{-1} in IR and Raman spectra besides $\delta(XO_4)$ modes cover valence and deformation modes of the two dif-ferent polyhedra AlO_n (n = 5 and 6); those involving the OH groups give partly strong INS signals in the same range. The component bands of the split $\nu(XO_4)$ vibrations (X = P, As) in the IR spectra are remarkably narrow; this fact may partly be due to the large distances of the anions in the crystal lattice (over 4.5 Å in **1**) and as a conse-quence to weak dynamical interactions of the vibrating anions.

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NORMAL COORDINATE ANALYSES OF RUTHENIUM SULFUR DIOXIDE COMPLEXES

P5.31

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In connection with previous work on sulfito, hydrogensulfito, and sulfur di-oxide complexes of platinum group metals [1-3], we carry out normal coordinate ana-lyses on cationic sulfur dioxide complexes *trans*-$[RuX(SO_2)(NH/D_3)_4]^+$ (X=Cl, Br, I) considering all H/D atoms to assist assignment of bands in the vibrational spectra and study connections between structural parameters and force constants (used pro-gramme [4]). The symmetry of the cations is assumed as C_{2v}-*mm*2.

The required experimental frequencies are taken from IR, FIR and Raman spectra of $[RuX(SO_2)(NH_3)_4]X$, $[RuX(SO_2)(ND_3)_4]X$ (X=Cl **1/1D**, Br **2/2D**, I **3/3D**), $[RuI(SO_2)(NH_3)_4]ClO_4$ (**4**) and $[RuI(SO_2)(NH_3)_4]_2SiF_6$ (**5**) [5,6]. Raman spectra of **3** and **4** could not be obtained due to decay of the samples in the laser beams (Ar^+, Kr^+) or heating-up (NdYAG), however, FT-Raman spectra of **3D** and **5** are available.

Under the assumed point group, four out of the five deformation modes of the pseudo-planar RuN_4 entity are allowed in the IR spectra. Under pseudo-symmetry D_{4h}-4/*mmm* of this fragment, two vibrations, E_u and A_{2u}, remain IR active. These vibrations are assigned to the strongest IR absorptions in the region between 300-200 cm^{-1}, *e g* for **2/2D**: 265/233 cm^{-1},sh, A_1; 244/221 cm^{-1},br, B_1, B_2. The agreement of calculated and observed frequencies is satisfactory (259/244 cm^{-1}, A_1; 247,250/222,224 cm^{-1}, B_1, B_2, for *trans*-$[RuBr(SO_2)(NH/D_3)_4]^+$). The similar frequencies of the A_1, B_1 and B_2 modes imply small *cis*-interaction force constants, which are ignored in the calculations. Small *cis*-interaction is generally found in this type of complexes. Force constants for NRuN deformation (129 N m^{-1}) are comparable with those in the related $[RuBr(NH_3)_5]Br_2$ (112 N m^{-1}) [6].

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P5.32

BONDING DATA FOR RHODIUM-NITROGEN BONDS AFFECTED BY THE *trans*-INFLUENCE OF SULFITO LIGANDS

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Recently, spectral data and force constants of Rh–N bonds were given for a compound with the anion *cis*-$[Rh(SO_3)_2(NH_3)_4]^-$ suggested by the spectral findings [1]. Since, the crystal structure of $Na[Rh(SO_3)_2(NH_3)_4]\cdot 2\,H_2O$ (**1**) confirmed this sug-gestion, and vibrational spectra of **1** and the deuterated **1D** were measured [2].

In **1** the anions approach symmetry C_{2v}–*mm*2. The short Rh-S bonds (mean $\bar{r}$(Rh-S) 227.3 pm) in *cis*-position lie opposite to Rh-N bonds ($\bar{r}_1$(Rh-N) 213.4 pm) lengthened by the *trans*-influence of the sulfito ligands with respect to the remaining Rh–N bonds ($\bar{r}_2$(Rh-N) 208.1 pm) *trans* to each other; this linear N-Rh-N fragment provides an internal reference for estimating the *trans*-influence of the SO_3 ligand.

Raman and IR spectra of **1** and **1D** indicate *cis*-configuration of the anion (*e g* doublets for $\nu_s(SO_3)$ and $\delta_s(SO_3)$). The two different $Rh(NH_3)_2$ groups (bent and linear) produce two doublets for $\delta_s(NH_3)$ (≈1300 cm^{-1}), doublets for $\nu(RhN_2)$ (bent, 441/419 cm^{-1}) in Raman and IR spectra, and a strong Raman (493 cm^{-1}) and a weak IR band (481 cm^{-1}) for $\nu(RhN_2)$ (linear). In **1D** the valence vibrations of the two RhN_2 fragments shift to 412/393 and 459/447 cm^{-1}. The strong structured Raman band system (≈350 to 200 cm^{-1}) comprises $\rho(SO_3)$, $\nu(RhS_2)$ and $\delta(RhN_4)$ modes.

For estimations of Rh–N force constants f_r the two different RhN_2 groups are treated as independent oscillators, as the *cis*-interaction constant for the coupling between these groups is probably small (cf. [3,4]). For the bent RhN_2 group (angle 86.2°) the valence vibrations $\nu_s/\nu_{as}(RhN_2)$ (443/421 cm^{-1}) yield the force constants f_{r1} 160 N m^{-1} and f_{rr1} 7 N m^{-1} (*cis*-interaction), assuming point-masses for the NH_3 li-gands. For the quasi-linear RhN_2 group (angle 178.8°) the valence vibrations $\nu_s/\nu_{as}(RhN_2)$ (496/483 cm^{-1}) give f_{r2} 211 N m^{-1} and f_{rr2} 35 N m^{-1} (*trans*-interaction). These force constants for Rh–N bonds with and without *trans*-influence are similar as in the complexes *fac*-$[Rh(SO_3)_3(NH_3)_3]^{3-}$ and *trans*-$[Rh(SO_3)_2(NH_3)_4]^-$ [3,4]; also the *cis*- and *trans*-interaction constants in the latter are close to those found here.

Thus, from both molecular structure and vibrational spectra quantitative data are available for the *trans*-influence of the sulfito ligand onto Rh–N bonds with refer-ence to unaffected Rh–N bonds in the same complex unit.

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VIBRATIONAL SPECTRA OF ALKALI METAL ISOOROTATES

P5.33

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Polycristalline samples of isororotic acid (5-carboxyuracil) and its alkali metal salts were studied by means of FTIR and FTRaman spectroscopy. For the acid, its low-temperature Ar-matrix IR spectra was also taken. The spectra were interpreted based on literature on uracile derivatives and theoretical calculations followed by PED analysis.

We were able to assign more than ten bands of the isoorotic system: $\nu(C_6\text{-}H)$, $\nu(C_5{=}C_6)$, ν(Ring Breath), $\beta(N_1\text{-}H)$, $\beta(N_3\text{-}H)$, $\beta(C_6\text{-}H)$, β(Ring), $\gamma(C_6\text{-}H)$, $\gamma(N_1\text{-}H)$, $\gamma(N_3\text{-}H)$ and for isoorotic acid in matrix also the $\nu(N_1\text{-}H)$ and $\nu(N_3\text{-}H)$ bands. The spectral picture of the carbonyl vibrations is, however, more knotty. There are three carbonyl groups present in the isoorotic system. All three vibrators stretching $\nu(C{=}O)$, three bending $\beta(C{=}O)$ and three out-of-plane bendings $\gamma(C{=}O)$ couples to each other. By analogy to the X-ray structures of known isoorotate complexes with Mn(II), Zn(II) and Fe(II) [1-3], one of them, the $C_4{=}O$ group, coordinates the metal atom or is hydrogen bond acceptor in the acid molecule and closes a six-membered chelate ring. Moreover, region of the stretching $\nu(C{=}O)$ vibrations is splitted by Fermi resonance typical for the uracil system. Thus for the deformation C=O vibrations only conservative assignement were done while the stretching C=O band were not interpreted.

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P5.34

CATION DISTRIBUTION AND THERMAL BEHAVIOUR OF THE FERRITE SPINEL $FeCo_2O_4$ STUDIED BY SPECTROSCOPIC TECHNIQUES

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In the last fifteen years a wide variety of spinel oxides, namely submicron ferrites have been synthesised by low temperature processes. The ferrite oxide powders resulting from decomposition of adequate precursors in a controlled reaction give rise to complex compositions spinels with mixed valences and a variety of M^{n+}- $M^{(n+1)+}$ pair occupying octahedral and/or tetrahedral sites. These compounds are of interest for their magnetic, thermodynamic and electrical properties and also for their catalytic and electrochemical behaviour.

We have prepared the $FeCo_2O_4$ spinel by coprecipitation technique using different temperatures for the final heat treatment. The samples obtained at 573K and then heated at 1173K are comparatively studied and we have followed the evolution of the crystal structure features as well as the cation distribution, particle size and morphology by several spectroscopic techniques.

XRD data show that the sample heated at 1173K, whose nominal composition is the same as the one prepared at 573K, has a well resolved spinel single phase. At 573K this spinel phase is already formed although different compositional phases are present, which point out that at this temperature different cation distribution are thermodynamic identical and stable, leading to the presence of similar but distinct cell spinel.

The XPS data and FTIR spectra support this statement and they are in accordance with the proposal of cation distribution given by ^{57}Fe Mössbauer spectroscopy for both $FeCo_2O_4$ samples prepared at 573K and 1173K, respectively. Nevertheless, SEM/EDS results do not show microdomains of different chemical composition for both samples.

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DISORDER EFFECTS IN THE VIBRATIONAL SPECTRA OF WOODHOUSEITES $MAl_3(OH)_6(XO_4)(YO_4)$

P5.35

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In our studies of synthetic minerals of the alunite and related types (repre-sentative $KAl_3(OH)_6(SO_4)_2$ (**1**)) [1], we are confronted with different kinds of disorder and their effects on vibrational spectra. Here, we discuss findings in Raman and IR spectra of woodhouseites, *e g* $CaAl_3(OH)_6(SO_4)(PO_4)$ (**2**) with statistical distribution of S and P atoms on crystallographically equivalent sites, *i e* disorder in these sites [2]; thus, **2** should formally have the same space group $R\bar{3}m$ as alunite (**1**) [3].

As to solid state spectroscopy this disorder has two effects: 1. The transla-tional symmetry gets fuzzy, consequently the $\vec{k} = 0$ rule as a basis for factor group analysis softens, *i e* transitions with $\vec{k} \neq 0$ should be possible. 2. An individual anion can have four different environments; therefore, also the site symmetry turns fuzzy, and lifting of degeneracies and/or activation of modes silent under sharp symmetry are expected. Thus, overlay of spectra of anions in different surroundings should cause broadening and splitting of bands.- To conclude the symmetry analysis for alunite [4] basically can be used but its softening has to be kept in mind.

The Raman spectrum of **2** astonishingly shows only one strong broadened band for $\nu_1(SO_4)$ and $\nu_1(PO_4)$ with broad companions assigned to the overlapping components of the ν_3 valence vibrations of both anions. The $\nu(OH)$ give a broad band in contrast to the two very sharp $\nu(OH)$ Raman bands of **1**. The low frequency part displays fewer and broader bands than **1** with obvious merging of analogous bands of the two anions. To avoid overlapping of anion bands the woodhouseites $CaAl_3(OH)_6(SO_4)(AsO_4)$ (**3**) and $CaAl_3(OH)_6(SeO_4)(PO_4)$ (**4**) were studied. The Raman spectrum of **3** shows separated but strongly broadened valence bands of SO_4 and AsO_4. Compared with **1** the 3 $\nu(SO_4)$ bands (1180, 1088, 1018 cm^{-1}) are unsystematically shifted by 10 cm^{-1} maximum. A δ-mode of the Al_2OH fragment (1120 cm^{-1}) is still observed in the same region. All $\nu(AsO_4)$ modes merge to a strong asymmetric band (885 cm^{-1}). In the low frequency range the broadened de-formation modes ν_4 and ν_2 of SO_4 and AsO_4 can be recognized besides framework deformation bands which are all broader than in the Raman spectrum of **1**.

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P5.36

UV-VIS INVESTIGATIONS ON Co, Fe AND Ni INCORPORATED INTO SOL-GEL SiO_2-TiO_2 MATRICES

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Recently, we have found cobalt, iron and nickel containing sol-gel silica samples to be active in the catalytic synthesis of multiwalled carbon nanotubes [1]. While trying to explain the observed activity differences we realised that literature data concerning the co-ordination and electronic state of transition metals incorporated into sol-gel materials is scarce. In this contribution we use diffuse reflectance UV-VIS spectroscopy to investigate the valence shell structure of mono- and bimetallic Co, Fe and Ni sol-gel silicas and titanias.

The samples were synthesised by hydrolysing $Si(OC_2H_5)_4$ and $Ti(i\text{-}OC_3H_7)_4$ in alcoholous solutions of metal nitrates. The total metal content was always 5%, and the Si:Ti ratio was set to 1:1 in the composites. The fresh gels were dried under reduced pressure and calcined in air at 773 K. UV-VIS spectra were recorded on a PE Lambda 15 spectrometer. A few representative spectra are presented in Fig. 1.

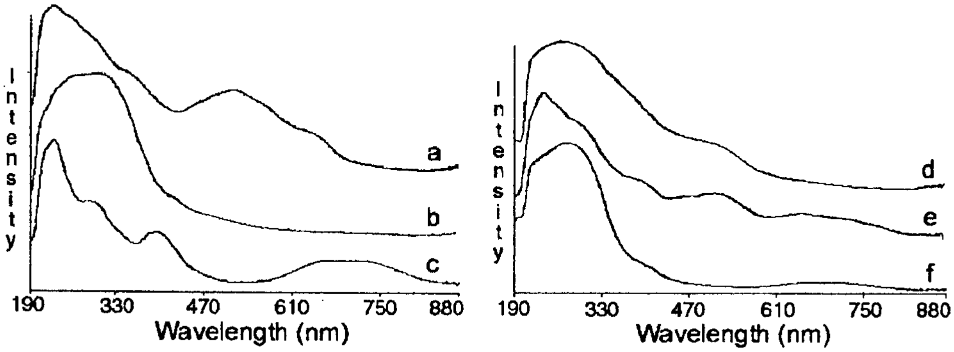

Fig. 1. – Diffuse reflectance UV-VIS spectra of sol-gel derived silicas containing Co (**a**), Fe (**b**), Ni (**c**), Co-Fe (**d**), Co-Ni (**e**) and Fe-Ni (**f**)

Spectra indicate that the co-ordination structure of the transition metals depends on the their type and the pre-treatment method, but is not related directly to the composition of the sol-gel matrix. Some peculiar features of the spectra of bimetallic samples seem to correlate with the enhanced catalytic activity of these materials. Our results suggest that fast, low-cost UV-VIS measurements can still provide useful structural information in the early stages of catalyst development.

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AN FT-IR AND UV-VIS STUDY ON THE STRUCTURE AND ACIDITY OF SOL-GEL DERIVED SILICA FOAMS

P5.37

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Recently, Bagshaw [1] described the synthesis of macrostructured mesoporous silicates (silica foams) utilising a non-ionic detergent (Triton N-101). These materials contain sub-millimeter sized pores easily visible even by an ordinary light microscope and have a very small apparent density. Apart from being interesting on their own right, such foams offer exceptionally high molecular diffusion rates and therefore could open new possibilities in the field of liquid phase heterogeneous catalysis. Of primary interest are materials containing Brönsted and Lewis acidic centres, as acid-base catalysis is one the major workhorses of the chemical industry.

Introducing active sites while retaining the foam structure is a challenging task. We prepared acidic foams by two different methods: (i) conventional impregnation of silica foams by heteropoly acid (e.g. $H_3PW_{12}O_{40}$) solutions, and (ii) one-step sol-gel synthesis [2] of the heteropoly acid – foam composite. This latter route has not been previously described in the literature.

In this contribution we use a Mattson Genesis FT-IR 1 instrument equipped with an *in situ* heatable vacuum cell to examine the acidity of the foams. The integrated differential intensities of the bands of adsorbed pyridine at 1540 cm^{-1} and 1450 cm^{-1} were taken as measures of the number of Brönsted and Lewis acid sites, respectively. The stability of the heteropoly acid incorporation was tested by washing the catalysts in a water:ethanol 1:1 mixture for 8 hours, after which the samples were dried and all spectra were recorded again. Structural investigations are based on characteristic features of the IR and diffuse reflectance UV-VIS spectra.

Our experiments revealed that the structure of the walls of the foams closely resembles that of ordinary sol-gel silicas. Although the presence of the heteropoly acid was confirmed both by IR and UV-VIS spectroscopy in every sample, no direct silica – acid links could be identified spectroscopically. The pyridine adsorption measurements proved that acid sites were indeed generated in the samples by both synthesis methods. The amount of acid sites can be tuned by changing the heteropoly acid contents of the impregnating solution (i) or the precursor gel (ii), respectively. Washing the foams in the polar solvent mixture, the majority of the active sites is removed in the case of the impregnated sample, but remains in the matrix in the case of the acidic foam synthesised by the new one-step sol-gel technique. Such stability is a major advantage when designing heterogeneous catalysts of good reusability, therefore we continue our research into this direction.

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P5.38

IR SPECTROSCOPIC STUDIES ON THE SURFACE CHEMISTRY OF MORDENITES MODIFIED BY CERIA

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Zeolites are regarded as acidic materials having both Broensted and Lewis acid sites in their pore system. It is also known that on the outer surface acidic sites can be found in non-negligible amount. These sites can deteriorate the selectivity of reactions. Suppressing acidity of the outer surface may be done by admixing cerium salt to the zeolite followed by appropriate heat treatment [1]. In this work changes in the acidity of mordenites and cerium-modified mordenites studied by IR spectroscopy are reported.

For the measurements NaMOR (Si/Al=19) and its Ce^{3+} ion-exchanged derivative CeNaMOR, HMOR (Si/Al=128) and its Ce^{3+}-modified (HMOR was impregnated with 30% cerium nitrate salt) form were used. Surface characterization was carried out by IR spectroscopy. Self-supported wafers were used in an *in situ* IR cell rendering treatment at different temperatures and in various gas atmospheres.

After treating the samples at 723 K in vacuum, from sample to sample different features were observed. Spectrum of NaMOR shows a sharp band at 3740 cm^{-1} and a broad absorption centered around 3650 cm^{-1}. The former band is attributed to the vibration of Si-OH groups sitting either on the outer surface or in the pores at vacancies. The broad band is associated with the extra-framework alumina species generally present in the zeolite after treatment at elevated temperatures. In the spectrum of Ce^{3+} ion-exchanged sample a new band was found at 3610 cm^{-1}, assigned to acidic OH groups generated by the Ce^{3+} ions.

On HMOR zeolite sample intensive bands were detected at 3735, 3692 and 3601 cm^{-1}. The band at 3735 cm^{-1} is due to the Si-OH groups present on the outer surface. At 3601 cm^{-1} the acidic OH groups absorb, while in-between, OH groups bound by the extra-framework alumina species are seen. On the CeHMOR sample the intensity of the Si-OH band at 3735 cm^{-1} decreased. It may be explained by the diminishing concentration of OH groups on the outer surface of the zeolite. The acidic OH absorption also vanished, while that due to extra-framework species became more pronounced. In accordance with the results obtained for OH groups, by pyridine adsorption the NaMOR sample proved to be non-acidic and HMOR showed only Broensted acidity. The Ce^{3+} ion-exchanged Na-mordenite has both Broensted and Lewis acid sites. Here the Broensted centres were observed even after evacuation at 673 K for 1 h suggesting the presence of very strong acid sites. Similar conclusion can be drawn in the case of Ce^{3+}-modified HMOR zeolite. However, the intensities of bands typical of Broensted sites decreased much faster with temperature in this case than for the Ce^{3+}-exchanged NaMOR sample.

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INTERCALATION OF VARIOUS OXIDE SPECIES IN-BETWEEN LAPONITE LAYERS STUDIED BY SPECTROSCOPIC METHODS

P5.39

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Using the conventional wet ion-exchange method Al-, Ti-, Cr-, V-, Ta-, Zr-, and Fe-oxide containing pillars can be generated by intercalation of polyoxometal cations formed from partially hydrolyzed solution of the appropriate metal salts. Starting from synthetic layered silicates such as rectorite instead of natural smectites like montmorillonite or natural hectorite results in more uniform materials of higher purity, since only traces of impurities or secondary phase contaminants are present.

We studied the preparation, characterization and application of rectorite pillared with Al, Zr, Ti, Cr, V, Fe and Ta-polyoxo cations. Results of these investigations are reported in this communication.

Pillared samples were prepared from rectorite synthesized in our laboratory by the procedure given in ref. [1]. The general aspects of the preparation method (OH/metal ion, aging time and temperature) has been published in [2]. Samples pillared with Ta-oxides was synthesized following the description given in [3].

The samples were tested by physical and chemical methods. IR-, UV-VIS spectroscopy, XRD and BET measurements were applied to characterize the intercalated structures. Pyridine adsorption monitored by IR spectroscopy was used to study the acidic character of the substances.

The pillaring procedure was successfully performed by each intercalation precursor. The cations of redox character were identified by UV-VIS reflectance spectroscopy. The thermal stability of the various specimens was satisfactory, since after heat treatment at 500 °C followed by rehydration, significant change was not observed either in the XRD patterns or the BET areas of the samples.

The results of acidity measurements allowed us to divide the samples into two main groups. Members of the first group (Al-, Cr-, Fe-oxide intercalated materials) were proved to be acidic, while only slight acidity was found for the Ti-, V- and Ta-oxide pillared substances. For samples having acidic character both Broensted and Lewis acid centres were found (pyridine bound to Broensted and Lewis centres results in the appearance of a band around 1540 and 1450 cm^{-1}, respectively).

Successful synthesis of PILC samples with high thermal stability was performed resulting in samples of completely different characteristics. Both acidic and non-acidic samples were found by pyridine adsorption monitored by IR spectroscopy

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P5.40

LOW FREQUENCY RAMAN SPECTRA OF A GLASS-FORMING IONIC LIQUID BASED ON THE CROCONATE ION

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Molten salts at room-temperature, that is, *ionic liquids*, have been investigated in the last twenty years as alternative solvents for clean synthesis, catalytic processes and aluminium electrodeposition.[1] The croconate anion (Fig. 1) is one member of the oxocarbon ions, which are cyclic planar species with general formula $C_nO_n^{2-}$ (n=3,4,5,6).[2] In this work, a viscous ionic liquid with a glass transition temperature (T_g) at 20°C has been obtained from tetra(n-butyl)ammonium croconate. According to the Angell's classification of supercooled liquids,[3] the system has been characterized as a *fragile* one, that is, a liquid whose viscosity follows a steep (non-Arrhenius) curve at temperatures close to T_g. Low frequency (5–250 cm^{-1}) depolarized Raman spectra have been obtained from 360 K down to a deep supercooled state at 77 K. As shown in Figure 2, the so-called boson peak has been observed as long as the system is cooling below T_g, which is a characteristic feature of fragile liquids.[3]

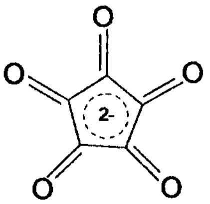

Figure 1. The croconate ion.

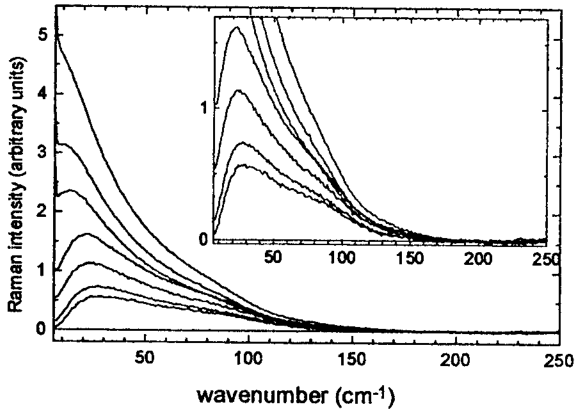

Figure 2. Depolarized Raman spectra of tetra(n-butyl)ammonium croconate at 293, 273, 250, 200, 150, 100 and 77 K (from top to bottom). The inset highlights the low temperature spectra.

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THE FTIR STUDIES OF THE BOROPHOSHOSILICATE SOLID SOLUTIONS CONTAINING ALKALI IONS Na^+ AND Li^+

P5.41

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The pure borophosphosilicate materials in amorphous and crystalline forms were synthesised by sol-gel method. The IR spectroscopic and X-ray studies allowed to find out the structure of solid solution of BPO_4 in SiO_2, in samples containing up to 10% mol. BPO_4.

The amorphous samples containing Na^+ and Li^+ ions as addition, were examined by FTIR spectroscopy. The changes in bands intensity and positions enable to draw some conclusions. The alkali ions Na^+ and Li^+ probably act as depolymerizators of borate and phosphate networks. There is also no evidence of boron coordination changes, from trygonal to tetrahedral. Concurrently, the silicate network is left unchanged.

The bands due to the vibrations of B-O bonds are not observed in the IR spectra of crystalline, obtained by devitryfication samples of composition analogous as amorphous ones. Such bands are present in the spectra of crystalline alkali free samples of the same BPO_4 content.

P5.42

IR AND ESR STUDIES ON SOME LITHIUM-BORATE GLASSES WITH VANADYL IONS

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Vanadyl ion VO^{2+} incorporated in glasses as a spectroscopic probe has been studied by several researches in order to characterize the glass local structure.The VO^{2+} ion provide information about many particular aspects like the geometry of structural units of the glass network, the character of chemical bonds in glasses as well as the coordination polyhedra (local symmetry) of transition metal ions [1].

IR and ESR studies were performed on $xV_2O_5(1-x)[2B_2O_3 \cdot Li_2O]$ glasses system ($0.5 \leq x \leq 50$ mol %) in order to obtain information on the influence of V_2O_5 content on the local symmetry and interaction between vanadium ions in lithium-borate glasses.

IR spectra contain the absorption bands characteristic for $2B_2O_3 \cdot Li_2O$ glass matrix and V_2O_5 oxide. The two ν(B–O) stretching vibrations at 1250 cm^{-1} and 1070 cm^{-1} indicate the presence of both B^{3+} and B^{4+} ions in the B_2O_3 oxide. The low intensity band at 415 cm^{-1} is due to ν(Li–O) stretching vibration. V_2O_5 oxide determines the appearance in the IR spectra of two absorption bands at 1070 cm^{-1} (ν_{as}(V=O)) and 950 cm^{-1} (ν_{as}(V–O)). Owing to the polyvanadate (clustered) ions formation by increasing the V_2O_5 content, the intensity of the ν_{as}(V–O) band increases, while the intensity of the ν_{as}(V=O) band decreases. The appearance of B–O< stretching vibration ($\approx$ 1400 cm^{-1}) at lower wavenumber than in crystalline B_2O_3 confirms the amorphous nature of these glasses. The variation of the $A_{\nu(V-O)}/A_{\nu(B-O-B)} = A_{950}/A_{700}$ ratio versus x (V_2O_5 mol %) show that the number of V=O bonds is slowly modified with the change of the glass composition. The x dependence of the $A_{\nu(V=O)}/A_{\nu(V-O)} = A_{1070}/A_{950}$ ratio suggest that the number of V=O bonds increases more rapidly than the number of V–O bonds.

ESR spectra obtained at room temperature for glasses with small content of V_2O_5 ($x \leq 5$ mol %) show a well resolved hyperfine structure typical for isolated vanadyl ions in a ligand field of near octahedral (O_h) symmetry. For $x > 20$ mol % the ESR spectra may be considered a superposition of two signals: one with a resolved hyperfine structure typical for isolated VO^{2+} ions in a C_{4v} symmetry and another broad line without structure at $g \approx 1.96$ for associated vanadium ions. The clustered ions are due to the dipole-dipole interactions between V^{4+} ions and their number increases with the V_2O_5 content. The V_2O_5 becomes a former of the network at high concentration ($x > 20$ mol %) together with B_2O_5.

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FTIR, UV-VIS AND EPR INVESTIGATIONS OF MULTICOPPER POLYOXOTUNGSTATES WITH Bi(III) AS HETEROATOM

P5.43

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Polyoxometalates (POM) incorporating different metallic ions often have utility in medicine, catalysis, material science and biology [1]. The lacunary polyoxometalates containing Bi(III) as heteroatom reveal interesting structural properties because of the pair of electrons of the Bi(III) atom, sterically-inert or active in α(β)-B Keggin isomers. However this fact favorises the coupling of trivacant β-B–BiW_9O_{33} or α-B–BiW_9O_{33} fragments through different number of Cu(II) ions [1].

Three Cu(II)-POM complexes, containing two, three and four Cu(II) ions respectively were investigated by spectroscopic (FTIR, UV-VIS, EPR) methods: $Na_8[Bi_2Cu_2W_{20}O_{68}(OH)_2(H_2O)_6]\cdot 26H_2O$ (**1**), $Na_{12}[Cu_3(BiW_9O_{33})_2(H_2O)_3]\cdot 29H_2O$ (**2**) and $Na_{10}[Cu_4(BiW_9O_{33})_2(H_2O)_2]\cdot 43H_2O$ (**3**).

The $\nu_{as}(Bi–O_{b,c}–W)$, $\nu_s(W–O_b–W)$, $\nu_{as}(W–O_c–W)$ stretching vibration bands are more affected by the coordination of Cu(II) ions at $O_{b,c}$ type oxygen from the β-B–BiW_9O_{33} units (in **1**) and α-B–BiW_9O_{33} units (in **2** and **3**). The $\nu_{as}(W=O_d)$ frequency is unchanged in the Cu(II) complexes FTIR spectra comparative to the ligands spectra, a sign of the structural stability of trilacunary Keggin units. The lone-pair electrons on each bismuth atom are sterically-inert in **2** but sterically-active in **3**.

The ligand to metal charge transfer $p_\pi \rightarrow d_\pi$ transitions in the W=O bonds is shifted for **2** ($\approx 700\ cm^{-1}$) and **3** ($\approx 946\ cm^{-1}$) comparative to $Na_9[BiW_9O_{33}]$ ligand and for **1** ($\approx 350\ cm^{-1}$) comparative to $Na_{12}[Bi_2W_{22}O_{74}(OH)_2]$ ligand. The broad d → d transition bands in the visible region of the electronic spectra correspond to Cu(II) ions in C_{4v} symmetry (for **2** with CuO_4O^* chromophore) or distorted O_h symmetry (for **1** with $CuO_3O^*_3$ local unit and for **3** with CuO_6 and CuO_5O^* local units).

The axial powder EPR spectrum of **1** ($g_{\parallel} = 2.267$, $g_{\perp} = 2.013$) could be explained by considering noninteracting Cu(II) ions and $S = 1/2$ ground state. The copper ions are coupled in **2** and **3**, the EPR spectra being explained with $S = 3/2$ and $S = 2$ effective spins respectively. Te corresponding ZFS axial components ($D = 0.0212\ cm^{-1}$ for **2** and $D = 0.0144\ cm^{-1}$ for **3**) are in good agreement with that of the other POM with three and four exchange coupled Cu(II) ions [2].

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P5.44

VOIDS, AMORPHOUS AND CRYSTALLINE PHASES INFLUENCE ON POLYSILICON ENERGETIC STRUCTURE

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The Effective Medium Approximation (EMA) [1] is a usually method for estimating the dielectric response for a mixture (in our case polycrystalline silicon compound by crystalline silicon-cSi, amorphous silicon-aSi and voids). From refraction index n and absorption constant k spectra (calculated with this method) is possible to evaluate by Tauc [2] and Cody [3] models the value for optical bandgap for the material taking into account that it is non-crystalline.

C-Si structure can be modifying by a-Si and voids introducing. So, the optical properties are changed because another phase into c-Si introduce the disorder, or it can said appear an extended defect in c-Si. From $\sqrt{k}$ versus (hω) (Cody [3]) or 1/ hω (Tauc [2]) by a linear fit were evaluated the value for optical bandgap E_g. In both models does make the assumption that the density of state is responsible of spectral dependence of absorption index (which depends on absorption coefficient by the relation $\alpha = 2k\omega / c$).

The voids, a-Si and c-Si percents were varied in the range of real percents observed in polycrystalline silicon. Firstly, the c-Si percent was kept constant and it was varied the voids and a-Si percents. The same calculation was performed for different c-Si percents.

The investigated energy is in the range of 1.65 eV to the edge of fundamental absorption. The formula for absorption coefficient demonstrated by Tauc and Cody fit the simulated spectra for k.

The optical bandgap calculated with both Cody and Tauc models are presented The influences of different phases percent variation to optical properties are discussed. The obtained results for $\sqrt{k}$ and E_g are in a good agreement with the literature [4].

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INFRARED SPECTROSCOPIC STUDY OF BENZENE AND CHLOROBENZENE ADSORPTION ON Pt,Cu- AND Pt,CoZSM-5 BIMETALLIC ZEOLITE CATALYSTS

P5.45

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There are several experimental methods for monitoring the adsorption energies of adsorption sites on various zeolites. For the determining the strength distribution of different adsorption sites spectroscopic methods are generally applied using probe molecules. The aim of the present work is to study the adsorption behaviour of benzene and chlorobenzene in bimetallic zeolite systems in order to map the strength distribution of adsorption centers.

The CuZSM-5 CoZSM-5 and PtZSM-5 samples were prepared by ion-exchange of NaZSM-5 at room temperature in solution of $Cu(NO_3)_2$, $Co(NO_3)_2$, and $[Pt(NH_3)_4](NO_3)_2$, respectively. For producing Pt,Cu- and Pt,CoZSM-5 bimetallic samples, the monometallic specimens were further exchanged in a solution of $[Pt(NH_3)_4](NO_3)_2$ complex.

Infrared spectroscopy was used (i) to check the generation of framework vacancies upon various treatments applied, (ii) for acidity measurements using pyridine as probe molecule and (iii) to investigate the strength of adsorption sites by benzene and chlorobenzene adsorption.

The acidity of the samples were gradually influenced by the pretreatment condition. Upon reduction with H_2 the samples show mainly Broensted acidity, while reduction by $NaBH_4$ did not generate Broensted acid sites and only slightly modified the concentration of Lewis sites.

For the hydrogen forms of zeolites, the shift in the frequency of acidic OH groups due to the perturbation of their vibration by adsorbed benzene, is regarded as a measure of the strength of Broensted acid sites. The OH band, generally appearing around 3610 cm^{-1}, was shifted by 80-300 cm^{-1} on the H_2-reduced samples, depending on the nature of the cations.

Modification occurring in the vibrational state of the benzene molecule upon the adsorption on metal ions in the zeolites results in changes in the IR spectra. The energy of the degenerated C-C stretching bands found in benzene vapour at 1482 cm^{-1} is split to more than two bands due to the different adsorption centers.

When chlorobenzene was adsorbed similar changes could be detected, however, there were differences in the shifts of the bands.

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P5.46

THE SPECTROSCOPIC STUDIES OF THE MIDDLE RANGE ORDER IN NATURAL ZEOLITES

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In the paper, the use of the precise interpretation of the middle infrared range (MIR) spectra as a source of information on the middle range order in the natural zeolites structure is shown. The middle range order is connected with the presence of rent members ring systems, creating so-called SBU (secondary building units). The proper identification of these units is so important because it is one of the main criteria of zeolites division to particular structural groups. In the MIR spectra, the rigs built up of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra possess bands in the range of pseudolattice vibrations e.g. within the range 500-800 cm^{-1}.The appearance of the bands in the given range can be treated as an indicator of the presence of "over-tetrahedral" structural order. The vibrations corresponding with the bands described above, differ from the typical lattice vibrations connected with the long range order. The bands due to the lattice vibrations are located in the far infrared range e.g. below 400 cm^{-1}.

In the pseudolattice vibrations range the shape of spectra is complicated because of a great number of bands coincidence. The proper band assignment was possible after the earlier decomposition of the bands to single components.

The obtained MIR spectra of zeolites were then compared with the spectra of cyclosilicates and framework silicates as well as aluminosilicates containing different number of ring members. The spectra measured in the helium temperature were also obtained in order to identify bands ue to pseudolattice vibrations. As additional, the studies in the far infrared range and also X-ray diffraction measurements were conducted.

THE CHARACTERISATION BY LUMINESCENCE SPECTROSCOPY OF URANIUM(VI) INCORPORATED INTO ZEOLITES AND ALUMINAS

P5.47

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There is currently considerable interest in the incorporation of the uranyl ion into solid matrices. This stems from the needs of incorporating nuclear wastes in inert solids for long-term storage,[1] the possibility of using excited uranyl ion as a photocatalyst[2] and the potential that uranium oxides have as efficient catalysts for the thermal degradation of pollutant molecules.[3]

We have incorporated uranyl ions into α- and γ-aluminas, and into the zeolites Y and ZSM-20 by adsorption from solution. These are retained by the solid and do not leach out when treated with water. In addition, a uranyl containing ZSM-5 has been prepared by chemical synthesis. These have been characterised by X-ray diffraction, scanning electron microscopy and vibrational spectroscopy. More detailed information on the site of uranyl incorporation has been obtained by luminescence spectral and lifetime measurements. Different behaviour was observed in α- and γ-aluminas, and the adsorbed species was found to depend on the counter-ion. In all cases using uranyl nitrate, a solid species $UO_3.xH_2O$ (schoepite) was identified. However, with the γ-alumina hydrolysed uranyl species were also observed to be present. On adsorption from uranyl acetate solutions, crystalline acetate species were present in addition to the hydrated uranium(VI) oxide. With zeolite-Y and ZSM-20, the luminescence studies confirm that there is formation of uranyl dimers within the zeolite cavities. For the synthesized ZSM-5 there were indications of a high degree of hydrolysis of the uranium(VI) species, which may have uranium bonded to silanol groups. The advantages of luminescence in characterising incorporated species in these systems will be discussed.

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P5.48

VIBRATIONAL STUDY OF SOME HOFMANN TYPE ANILINE CLATHRATES

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As a part of our study of Hofmann type clathrates, we have recorded the mid-infrared, far-infrared and Raman spectra of Hofmann type aniline clathrates. The investigated clathrates belong to a class of inclusion compounds with the general formula: $M(NH_3)_2M'(CN)_4 \cdot 2G$, where M is Ni, Cd, Fe or Mn, M' is Ni and G is aniline.

The main features in the infrared and Raman spectra have been assigned to (i) the vibrations of the aniline (guest) molecule and to (ii) the vibrations of the host lattice: $M(NH_3)_2M'(CN)_4$.

(i) The frequencies and shapes of the bands due to vibration of the enclathrate aniline molecule were compared to the ones in liquid aniline. A high frequency shift (between 5-15 cm^{-1}) was detected only for the bands due to C-H out of plane vibrations. This may indicate, as in the case of the benzene clathrates, a considerable host-guest interaction.

(ii) The bands due to the vibration of the host lattice were already assigned in our previous study of Hofmann type benzene clathrates [1]. In order to examine the vibrational spectra of the host lattice, we recorded a series of infrared spectra of these clathrates, in which the amount of the aniline molecules progressively decreases until eventually pure host lattice remains. It was found, as in the case of the Hofmann type benzene clathrates [2], that the abandonment of the guest molecules from the host lattice leads to changes in the structure of the "empty" clathrate.

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Spectroscopy of Surfactants Micelles & Liquid Crystals

THE COMPARATIVE STUDY OF DESTABILISATION EFFECT OF BOVINE SERUM ALBUMIN AND FATTY ACID – FREE BOVINE SERUM ALBUMIN ON PHOSPHOLIPID VESICLES.

P6.1

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The destabilisation effect of bovine serum albumin (BSA) and fatty acid free bovine serum albumin (BSAf) in concentration close to physiological level on bilayer lipid membranes has been examined. The influence of fatty acids on the stability of the albumin molecule has been well known [1] but their contribution to protein – lipid interactions is still discussed.

Liposomes from phosphatidylcholine – enriched fraction of deoiled soybean lecithin and cholesterol were prepared (similarly as previously [2]) by using the modified reverse – phase evaporation method. Liposomes were mixed and incubated 0.5h in room temperature or additionally about 24h at 4^0C with two kinds of albumin. The contents of lecithin and BSA in all 1ml samples were 0.5 mg and 30 mg respectively. Liposomes were separated from BSA by chromatography on Sepharose 2B-Cl column with 0.9% w/w NaCl with addition of 10 ml/1l 0.1 N NaOH buffer eluent, pH $\approx$ 7.5. We determined the amounts of lecithin and BSA in the collected fractions spectrophotometrically in terms of absorbance at 206 nm and 278.5 nm respectively (the absorption spectra were recorded on UV VIS spectrophotometer JASCO V-530).

We have received the elution profiles for gel filtration of liposomes and BSA separately and of liposome – albumin mixtures. Then we calculated the summary amounts of lecithin and albumin in liposomal and protein fractions respectively. The determined amounts of lecithin in liposomal fractions was smaller for liposome – albumin mixture in all cases. The comparison of elution profiles indicated disintegration of the liposomal membranes.

Our results show that both kinds of albumin lead to destruction of vesicles even after 0.5h incubation. Using t – test we received essential differences ($p < 0.05$) for the average lecithin content in liposomal fractions in the case of liposome alone gel filtration and liposome – BSA after 0.5h ($p = 0.0025$) or after 24h ($p = 0.0001$) incubation and liposome – BSAf after 0.5h ($p = 0.0205$) or after 24f ($p = 0.0051$) incubation. No statistically essential differences are observed between two studied kinds of albumin, although it seems that BSA destabilises liposomes stronger and faster than defatted albumin (BSAf). After 0.5h, BSA and BSAf dissolved about 27.7% and 18.8% of liposomes respectively. After additionally 24h incubation at 4^0C, about 36% of liposomes were destroyed in the presence of BSA and 28% in the presence of BSAf.

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P6.2

SOLVATOCHROMIC FLUORESCENT PROBES IN HOMOGENEOUS AND MICROHETEROGENEOUS SYSTEMS

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Aggregation of amphiphillic molecules in solution can produce a variety of structures, including micelles, microemulsions and liquid crystals. Elucidating the microstructure of these domains is vital for a detailed understanding of their macroscopic properties. We have been particularly interested in the phase behaviour of the non-ionic surfactant $C_{12}E_5$ ($C_{12}H_{25}(OCH_2CH_2)_5OH$) in the presence of water and an alkane. Mixtures of $C_{12}E_5$ and water can exhibit micellar, lamellar, hexagonal and cubic phases [1]. In the presence of oil, this three component system shows a variety of single-phase and two-phase regions [2]. Of particular interest are the microemulsion phases, which are the water continuous at low oil content and oil continuous at high oil content, but which can display bicontinuous phases depending on composition and temperature.

We have employed three solvatochromic probes, prodan, nile red and 4-di-1-asp, to monitor this phase behaviour using both steady state and time-resolved fluorescence techniques. These probes were first characterised in terms of their emission spectra and relative quantum yields in the component solvents of the ternary system. Other solvents of differing polarity and viscosity were also used to elucidate additional information. In the three component system these probes show different affinities for the various domains. In addition solvatochromic changes have been used to monitor the various phase transitions. Particular emphasis is placed on the nature and local composition of the bicontinuous phase. These solvatochromic studies are applicable to other microheterogeneous systems, including liquid crystal and sol-gel systems.

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P6.3

EPR STUDIES OF FOUR NEW SPIN LABELED NICOTINIC ACID DERIVATIVES IN LIPIDIC BILAYERS

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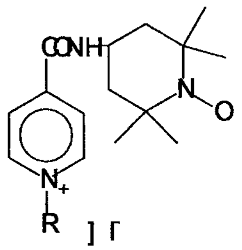
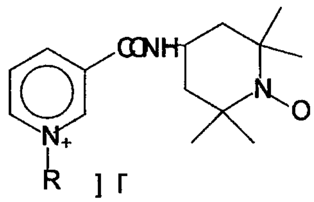
3-and 4-[N-4-(2,2,6,6-tertamethylpiperidinyloxy)]-carboxamide-1-R-(where R=methyl or R=dodecyl)-pyridinium-iodide free radicals were synthesized and investigated as new usefull spin labels.





X-band EPR spectra of all four compounds were studied in multilamellar liposomes. The spectra were analyzed by using a computer simulation for obtaining the characteristic magnetic parameters.

We investigated the influence on the EPR characteristics of: a) the alkyl chain R and b) the substituent position on the pyridine ring of the nitroxide moieties.

Both, the length of the alkyl chain and the substituent positions induce changes in the EPR parameters.

The interactions and the mobility of the compounds in multilamellar liposomes were derived from the magnetic EPR parameters.

P6.4

SPECTROSCOPIC INVESTIGATIONS OF DETERGENTS AND PROTEIN-DETERGENT COMPLEXES

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Cationic, anionic, zwitterionic and nonionic detergents are applied in the biosciences and in many (bio)technological processes. The structural investigation of protein-detergent complexes and their constituents is of fundamental importance for two reasons: First, a deeper understanding of the action of detergents on proteins and, second, the correct choice of detergents for a variety of experimental and theoretical problems (e.g., solubilization, denaturation and unfolding of proteins, interaction between detergents and proteins, binding studies, determinations of the molar mass, size and shape of protein-detergent complexes). In the past, mainly scattering and hydrodynamic data were reported, while spectroscopic approaches were applied only recently [1-3].

Spectroscopic methods (UV absorption, fluorescence excitation and emission, near- and far-UV circular dichroism) and physicochemical techniques that use absorption or fluorescence spectrographs merely as sensitive detector systems, e.g. for size-exclusion chromatography and analytical ultracentrifugation, yield a variety of molecular characteristics of micellar detergents and protein-detergent complexes. However, application of the given techniques requires a careful adaptation of the conventional techniques and, in addition, the consideration of various precautions.

Because of the low absorbance of nonaromatic detergents, labeling of detergent micelles by appropriate (fluorescent) dyes, such as N-phenyl-1-naphthylamine, was studied in detail. Solvatochromic pyridinium N-phenolate betaine dyes may be used as polarity probes to characterize the micelle/solvent interface. Since proteins usually possess aromatic residues, for the analysis of detergent-free proteins and protein-detergent complexes no labels are required. In order to interpret the data, discrimination between the signals of monomeric and micellar detergents and other (macro)solutes is important.

The results reveal many differences in the behavior of detergents and protein-detergent complexes. The spectroscopic methods monitor detergent-induced changes in the environment of protein aromatics which may lead to significant shifts of fluorescence intensity and maximum fluorescence emission, as well as differences in conformation and stability. The effects of different detergents reflect not only the chemical nature of the detergents, but also differences in the size and structure of micelles and their complexes. Apart from temperature and pressure, relevant parameters are the concentrations of the solutes, the ionic strength of the medium, among others.

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SPECTROSCOPY OF POTENTIAL SENSITIVE NLO-ACTIVE DYES IN LIPID MEMBRANES

P6.5

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A method (see Figure 1) is presented which allows the precise recording of membrane potentials using NLO spectroscopy of specially designed and synthesized dyes incorporated in a lipid double layer of hemispherical vesicles that serve as a model for biomembranes. The dyes are accumulated in the outer layer of the membrane and show large polarisabilities and hyperpolarisabilities which are responsible for the intensities of the SHG signal. This intensity is markedly dependent on the membrane potential (see Figure 2).

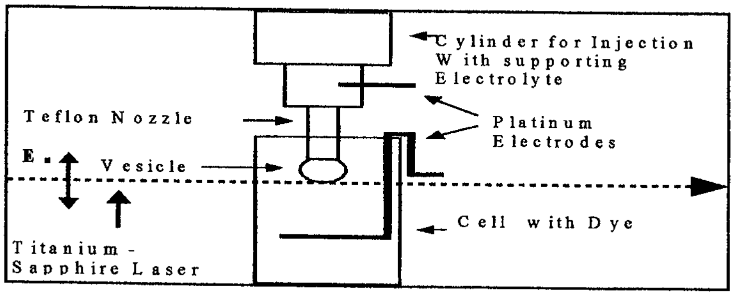
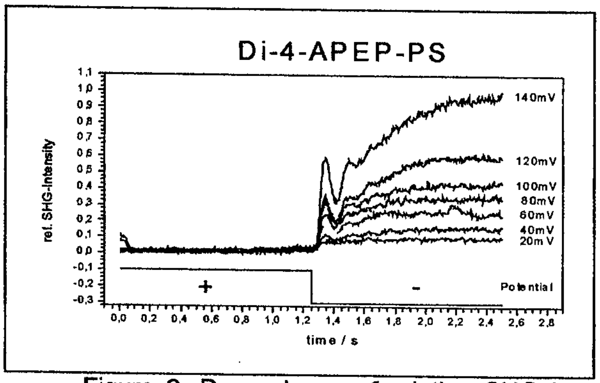


Figure 1. Arrangement of electrodes for generation of membrane potentials and direction of laser irradiation.



A detailed analysis and interpretation of the physical effects as well as a presentation of useful dyes are given.

Figure 2. Dependence of relative SHG intensity of dye *Di-4-APEP-PS* on membrane potentials varying from ± 20 mV to ±120mV (in 20 mV steps).

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P6.6

INFLUENCE OF GLUCOLIPIDS ON THE PHASE BEHAVIOUR OF PHOSPHOLIPIDS

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Glucolipids play a major role for the stabilisation of biological membranes and hinder the collaps of the bilayers in absence of water. To study the cryoprotective effect on a model system we have prepared mixtures of the well-investigated acyl chain deuteriated 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC-d62) and the glucolipids 1-O-hexadecyl-β-D-glucopyranoside(Glu1/0) and 1-O-(triethoxy-hexadecyl)-β-D-glucopyranoside (Glu1/3). By means of DSC and temperature variable ATR-FTIR spectroscopy mixtures of different amount of the glucolipid were investigated in the dry and the hydrated state. On the hand of the CH_2 and CD_2 symmetric stretching modes the chain flexibility can be monitored separately for both components. The behaviour of the polar lipid head groups can be studied on the carbonyl stretching frequency and the asymmetric PO_2^- absorption signal.

It was found that in the dry state the chain melting temperature approaches the phase transition temperature of the hydrated DPPC-d62 with increasing amount of Glu1/0 or Glu1/3. The CO and PO_2^- signals indicate that both functions are hydrogen bonded and the glucopyranoside is incorporated into the phospholipid layer. The shift of the PO_2^- signal due to the hydrogen bonding is comparable to that of the hydrated DPPC-d62.

In the presence of water the formed aggregates are still present but no significant lowering of the phase transition temperature compared to the dry state is observed.

DSC AND NMR ANALYSIS OF THE STATE OF WATER MOLECULES IN SOME POLYMERIC MEMBRANES

P6.7

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Study of water and water-glycerol solutions in AN69 membranes was made using scanning calorimetry (DSC) and NMR spin-spin relaxation methods. The recorded spectra indicate two thermal transitions, which were associated with the two different states of water inside the pores of membrane.

The study of the behavior of water molecules inside limited spaces, like the pores of polymeric membranes, is of a great interest because the special applications of these materials in biology, medicine, filtration of liquids [1,2].

Actually is widely accepted tat the water molecules introduced in the pores of polymeric membranes, can exist also in free state and bounded state, the fraction of these states depending on the solvent concentration [3]. The two states of water are characterized by different energies required for the melting process.

The DSC recorded spectra clearly indicate two transition phenomena, in the temperature range 270–285 K, which were associated with the two states of water inside the pores of membrane. These transitions depend on the water concentration inside the pores.

The relaxation of the transversal magnetization, observed by NMR method, is influenced by the presence of water molecules inside the pores [4]. The analyze of the experimental curves can indicate, in some cases, the existence of the two states of water.

The two methods, DSC and NMR, provides complementary informations about the state of water inside the pores of membranes.

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P6.8

IR-SPECTROSCOPIC CHARACTERIZATION OF PHOSPHOLCHOLINE HEADGROUPS IN MODEL MEMBRANES AND MODEL COMPOUNDS

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Lipids represent an important class of biologically essential molecules. Their most meaningful property can be seen in amphiphilicity, *i.e.* the coexistence of polar and apolar regions in one and the same molecule, enabling lipids to form supermolecular assemblies and aggregations. The polar domain of phospholipids can be assumed to play a major role in cell biology since (i) it possesses charges which may exert Coulombic forces against environment and (ii) it provides sites for the specific binding of potential partner molecules, be it from water as the natural medium or, competitively, other membrane constituents (proteins, sterols) and membrane-active compounds (peptides, drugs). FTIR spectroscopy is one of the most powerful and frequently used methods to characterize lipid systems on a submolecular level [1,2]. However, previous IR-spectroscopic studies were devoted mostly to the apolar region, see [1,2] and papers cited therein.

In order to get a more detailed insight into the lipid-headgroup structure, we have studied solid deposits of a number of selected lipids and lipid models. Dimyristoylphosphatidylcholine (DMPC) and its deuterated analogues, d4-DMPC and d54-DMPC with labelled methylene groups in headgroup and acyl chains, respectively, were chosen as lipids, and methylphosphocholine (MePC), choline and acetylcholine as lipid models. Alltogether, these substances allow for a more or less discrete consideration of the PC headgroup and its sub-moieties. Water activity was taken as a variable to create changes in headgroup structure.

Although all the three lipid models are able to imbibe substantial amounts of water, they respond distinctly different to hydration. Whereas the IR-active groups of choline and acetylcholine obviously remain largely unaffected, many of the spectral parameters of MePC undergo drastic changes. This refers to the key role that the phosphate unity plays in lipid-hydration processes, cf. [2] and references therein.

The set-up with DMPC and its deuterated analogues makes possible to follow the hydration-induced spectral implications concerning the methylene groups of headgroup and chains separately. The observed phenomena are discussed in relation to both the lyotropic chain-melting transition occurring in DMPC and its analogues and the strong water binding to phosphate.

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TWO-COMPONENT SPIN LABEL EPR SPECTRA IN GRAMICIDIN S / DIMYRISTOYLPHOSPHATIDYLCHOLINE COMPLEXES IN FLUID PHASE BILAYER

P6.9

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The association of spin labelled lipids in gramicidin S / dimyristoylphosphatidylcholine complexes has been studied using EPR spectroscopy with its unique time scale at 25-65 C. In a limited range of temperature in the fluid phase of lipids, two-component spectra were observed which were assigned to motionally restricted lipids at the hydrophobic interface of peptide molecules and rapidly tumbling and diffusing lipids in peptide-free fluid phase lipid regions. The two populations of lipids were in rapid exchange due to lateral movements, and from van't Hoff plots the activation energy of such two-site lipid exchanges was determined. At 55 C the motionally restricted component lost intensity, and the effective correlation time of the fluid component suddenly increased. The time scale of nitroxyl spin label EPR (3×10^{-9} s) distinguishes the motionally restricted component as a rigid-limit-component only in the temperature interval of 25-55 C, but the two components merge into sharp 3-line isotropic spectrum as soon as the tumbling rate of peptides of small molecular weight is comparable to lipids.

P6.10

MIR AND NIR SPECTROSCOPIC STUDY OF POROUS MATERIALS FILLED WITH n-ALKYLCYANOBIPHENYLS

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Investigations of heterogeneous liquid crystal systems attract great interest for recent years because LCs in these systems show new physical properties which cannot be observed in pure LCs. Examples of such systems are LC incorporated in porous matrices (porous glass, molecular sieves, polymer matrices) or suspensions of LC with inorganic aerosil type particles.

We report on MIR and NIR spectroscopic studies of filled porous matrices. The homologeous series of n-alkylcyanobiphenyls (nCB) $CH_3\text{-}(CH_2)_{n-1}\text{-}(C_6H_4)_2\text{-}C{\equiv}N$ (n is a number of carbon atoms in alkyl tail, $n=2\div9$) has been used as a filler. All these nCB have a nematic LC phase, whereas 8CB and 9CB have a smectic one, too. Porous glasses with random location of pores (of 2-90 nm in diameter) and aluminosilicate mesoporous MCM-41 type molecular sieves with a regular arrangement of hexagonal channels (of 4-5 nm in diameter) have been used as hosts.

The dependences of the porous matrices filling level with nCB molecules on preparation and thermal pretreatment of porous matrices as well as on LC incorporation methods (from solvent, in nematic LC phase, from isotropic liquid) have been obtained.

It has been discovered that a part of nCB molecules interacts with active centers on pore surface creating a system of Si (Al)-OH···N≡C type H-bonds. This process leads to the change in shapes of the C≡N vibration bands: stretching (about 2226 cm^{-1}) and deformation (about 850 cm^{-1}) ones. We also found decreasing or complete disappearance of IR absorption related to stretching vibration of "free" OH group and its overtones in the spectra of filled porous glasses, and shift of H-bonded OH group stretching vibration band in molecular sieves and porous glasses.

The analysis of Q(C≡N) band components revealed the dependence of the number of LC molecules interacting with pore surface on the alkyl chain length and pore diameter.

CALCULATION OF VIBRATIONAL SPECTRA FOR CYANOBIPHENYL LIQUID CRYSTAL

P6.11

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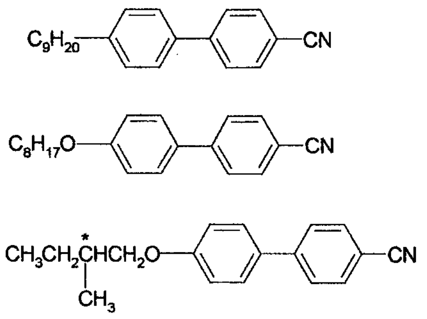
Harmonic vibrational frequencies for nematic and smectic cyanobiphenyl liquid crystal molecules (C15, M24 and K27) were calculated using semi-empirical PM3 and DFT method (B3-LYP/6-31G*).



K27

M24

C15

Figure 1. Structure of the cyanobiphenyl liquid crystal molecules.

The scaled quantum mechanical method (SQM) [1] was applied to density functional force field, for better reproducing the vibrational spectra. The additional scaling factor for C≡N stretching bend was optimised for training set of 10 molecules with C≡N group. Our simulated SQM spectra were successfully compared with the experimental IR data.

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P6.12

POLARIZED FT-IR SPECTRA OF BENZYL AND BENZOPHENONE ORIENTED IN THE NEMATIC LIQUID CRYSTAL 4-ALKYL- 4'-CYANOBICYCLOHEXYL

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Benzyl and Benzophenone dissolved and oriented in the nematic liquid crystal host ZLI-1695 (4-alkyl-4'-cyanobicyclohexyl) were studied by means of the polarization FT-IR spectroscopy. IR polarized spectra of molecules oriented in nematic liquid crystal can provide useful information on the symmetry properties of the vibrational transition. Orientation models of the solute molecules in the nematic solvent are proposed. Some previous assignments are rediscussed and corrected.

MOLECULAR ORIENTATION OF THIN ORGANIC LAYERS STUDIED BY FTIR-SPECTROSCOPY

P6.13

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Organic materials get more and more relevance in many fields of high technology. New substances sythesized under various aspects of application have interesting properties: they show a photo- or electro-luminescent behaviour, are liquid-crystalline, are used in non-linear optics and, prepared as thin films, they find new applications in microsystem technique, nano-technology and microsensorics.

In many cases molecular order determines the properties of thin organic layers.

FTIR-spectroscopy is one of the methods suitable to gain information about molecular orientation in highly ordered thin layers. The present paper deals with thermally induced changes of the molecular architecture in Langmuir-Blodgett multi-layers of an amphiphilic oxadiazole (Fig.).

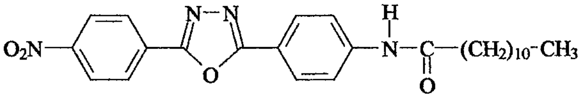

Fig.: Chemical structure of the investigated oxadiazole compound

The FTIR-spectroscopic investigations combining reflection absorption spectroscopy (RAS) and transmission spectroscopy with polarized radiation reveal changing absorbances of the LB-films in the temperature range from 20 °C to 250 °C.
At room temperature hydrogen bonds between amide groups of neighbouring molecules influence the layered structure to a great extent. The H-bonds are destroyed by thermal treatment. This process is accompanied by modifications of the spatial arrangement of characteristic molecular parts. Changes of the orientation of transition moments belonging to various molecular groups, e.g. to the NO_2-headgroups, the aromatic system and the CH_2-tail, indicate a laterally anisotropic organisation of the films between 100 °C and 200 °C. Annealing above 200 °C results in nearly isotropic molecular arrangement. Starting at 230 °C thermal decomposition of the oxadiazole film material is observed.

The molecular orientation in thin LB films can be determined, if the experimental band intensities of reflection-absorption and transmission measurements are compared. Based on a method developed by Umemura et al. enhancement factors for the reflection-absorption to transmission intensities of isotropic films were calculated. By use of these theoretically determined factors and experimental intensity ratios first results concerning orientation angles of selected molecular groups were obtained.

P6.14

A NOVEL PHOTO-ACTIVE SYSTEM: AZOBENZENE DERIVATIVE - LIQUID CRYSTAL. SPECTROSCOPIC STUDY OF KINETICS AND APPLICATIONS.

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Spectroscopic study of the *trans-cis* photoisomerisation of 4-fluoro-4'-methoxyazobenzene dissolved in pentacyanobiphenyl (5CB) was performed. The photoisomerisation kinetics was measured spectrophotometrically. The forward (*trans-cis*) reaction occurs upon UV irradiation (λ = 360 nm), whereas the reverse process can be driven thermally and/or photochemically (λ = 440 nm). The rate constants were determined at temperatures of stability of the nematic and isotropic phases of 5CB, and at the temperature of the nematic-isotropic phase transition. The photoisomerisation of azobenzene derivatives is known to be a first-order kinetic process [1,2]; nevertheless, deviations from the first-order kinetics were observed in the system under study, apparently associated with the nature of the matrix.

We prepared a tin cell consisting of two conductive glass plates (ITO-coated) with planar alignment of the nematic liquid crystal [3]. Azobenzene-doped liquid crystal was used as an active media. The cell was employed as an element for real-time holographic processing. We describe the origin of the diffraction gratings (holograms) induced by light intensity pattern. The mechanism is associated with changes of the order parameter in the liquid crystal matrix due to the photochromic reaction occurring in the guest molecules. Design and characterization (response time, diffraction efficiency) of the optically addressed spatial light modulator (OA SLM) is presented.

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STUDY OF NEMATIC LIQUID CRYSTALS CONFINED IN MOLECULAR SIEVES

P6.15

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The dynamical behaviour of liquid crystals (LCs) confined to restricted geometries has received considerable attention from both theoretical and experimental points of view. Previous work was focused on confining geometries having planar, cylindrical or spherical cavities. However, till recently, the molecular sieves were not used as host materials for LCs despite their high internal surface area, their chemical as well as mechanical stability.

In this contribution we present some results concerning the orientational dynamics of two related nematic liquid crystals (LC), 4-octyl-4'-cyanobiphenyl and 4-pentyl-4'-cyanobiphenyl, confined to the molecular sieves of MCM-41 and cloverite type. The former presents the smallest size of the pores used up to now for confinement, namely 20 Å, whereas the latter offered its (pores and) supercages of ca. 30 Å. The investigations were performed in a wide temperature range by dielectric spectroscopy, thermal analysis and FTIR spectroscopy.

Finely grounded molecular sieve powder was pressed in self supported pellets of ca.100 μm thickness. The pellets were evacuated at 300°C to remove water and other volatile impurities. Two methods were used to load the molecular sieve pellets with LC molecules. The LC content was found to be ca. 50% or even higher for samples loaded by method A, and 40 %, as it may be hosted by pores, for samples loaded by method B.

Randomly oriented grains of our sieves have an overall randomizing effect on the nematic director, namely the so called quenched disorder leads to lowering of the transition temperatures, rounding and lowering of the heat capacity peak and may change the transition order. As expected, the phase transitions of the bulk LCs cannot be detected for the molecules confined inside the pores. A new slow relaxational process occurs in the whole temperature range due to the motions of the molecules in the layer at the pore walls; the temperature dependence of the characteristic frequency obeys a Vogel-Fulcher-Tamman (VFT) law associated to a glassy state. The orientational order within the small pores is mostly dominated by the local environment.

At variance of the MCM-41 material, the cloverite was proved to be a veritable host for the LC, due to its supercages, typical LC phase properties still exist after loading. Therefore, the system cloverite-LC might be a new material.

FTIR measurements show the interaction of LC molecules with the acid (Lewis and Brönsted) sites of the molecular sieves.

P6.16

ORIENTATION ORDERING AND CONFORMATION EQUILIBRIUM IN THIN INTERLAYERS OF NEMATIC LIQUID CRYSTAL — PENTYL-CYANOBIPHENYL

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The orientation behaviour of alkylcyanobiphenyls has been a subject of considerable attention, because the molecular orientation controls their electro-optical properties. In practical applications, such liquid crystals are mainly used in a thin film state. A number of theoretical researches indicates that the molecular structure and orientation behaviour in thin films are strongly affected by both the properties of media confining the liquid interlayer and the thickness of interlayer. As regards to the experiments, for systems containing liquid crystal films, the above influence has not been extensively studied.

In the present work we explored the capabilities of polarized infrared spectroscopy for the study of orientational and conformational microstructure of pentyl-cyanobiphenyl (5CB) thin symmetric interlayers, confined by crystalline fluorite substrates. Using a specially developed spectroscopic cell, we have registered the alteration of transmittance spectra in the course of interlayer thinning in the range from tens of microns to tens of nanometers.

To analyse the data obtained, we have cosidered two-fractional model, taking into account angular and directional ordering of molecular directors. The orientation function of byphenyl unit was evaluated from relative intensity of CN stretching vibration, and that of terminal methyl group was estimated from dichroic ratios of the symmetric and asymmetric stretching vibrations of the methyl group. The orientation of the latter was discussed in relation to the conformation of the alkyl chain.

Acknowledgements:The work was performed with financial support by Russian Foundation for Fundamental Research (grant # 98-03-32732).

STRUCTURAL INFORMATION FROM REDUCED IR-LD SPECTRA OF SUBSTANCES ORIENTED IN NEMATIC MESOPHASES

P6.17

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The orientation of substances in nematic liquid crystals of alkilbicyclohexyl type turned out to be a very useful technique for studying their IR linear dichroic (LD) spectra and polarization Raman spectra. The orientation in the IR technique is achieved by rubbing the inner faces of the IR cell windows in one direction while a very effective alignment of the nematic solutions for polarization Raman spectroscopy arrives at introducing the sample in a capillary tube of small inner diameter, e.g. of 0.3 mm.

IR-LD spectra obtained for parallel and vertical orientation of the polarization plane with respect to the nematic director are converted into reduced spectra by means of an interactive subtraction. Reduced spectra of symmetric molecules serve unequivocally for assignment of the symmetry appurtenance of their IR bands. The directions of some vibrational transition moments can be determined from the reduced spectra of molecules with a slight asymmetry. Overlapped bands and accidentally degenerated vibrational transitions are easily detected from their reduced spectra. Finally, Fermi-resonance doublets could also be identified this way. Entirely symmetric molecules can also give rise to LD if they strongly interact with the nematic solvent.

Polarized Raman spectra of substances oriented in anisotropic solvents can in principle yield the same information about molecular symmetry as IR spectra do. Their interpretation is, however, complicated by the necessity to operate through the polarizanility tensor.

Polarized IR and Raman spectra of aromatic hydrocarbons and aldehydes are presented as examples for the contribution of the reduced spectra to elucidation of symmetry and structure.

Spectroscopy and Molecular Structure

-Simple Organic Molecules
-Complexes

SPECTROSCOPIC STUDY OF MALONDIALDEHYDE DERIVATIVES

P7.1

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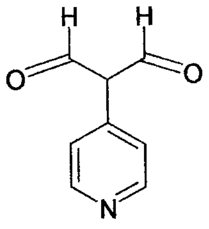
Malondialdehyde is one of the most significant of the wide range of metabolic and deteriorative products of lipid damage. Its formation during food processing and storage is widely used in quality control [1]. It is also of great carcinogenic or mutagenic interest because of its possible interaction with free amino acids, proteins, nucleic acids and amino phospholipids [2]. The aim of this study was to investigate the potential ability of 4-pyridyl- and phenyl- malondialdehydes (I, II) to complex substances containing amino groups.

It is clear from the UV spectra that three forms of I or two forms of II are present in the solution depending on the pH. ^{1}H and ^{13}C NMR, IR and Raman spectroscopic techniques were used to explain the structure and behaviour of these substances in water and DMSO solutions. The effect of addition of amines, some amino acids and their hydrochlorides on the spectra was compared with the effect caused only by the pH change.



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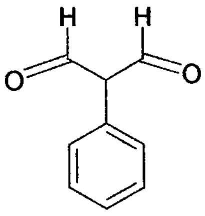

II

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P7.2

VIBRATIONAL SPECTRA OF CALIX(4)RESORCINARENE ISOMERS

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Calix(4)resorcinarenes are a class of substances with a potential at creating selective ion channels in artificial biomembranes [1]. If calix(4)resorcinarenes are synthesised from simple aromatic ring compounds, cone isomers with cis-cis-cis, cis-cis-trans and cis-trans-trans configurations can be observed. Besides that, so-called cone, chair and boat conformers of calix(4)resorcinarene can be observed [2].

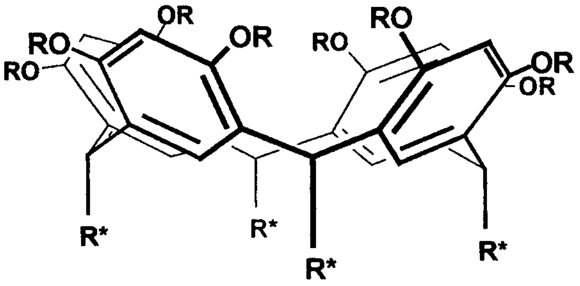

Fig.1. Cis-cis-cis isomer of calix(4)resorcinarene, R = -CO-CH_3, R* = -Phe-O-CO-CH_3.

Only the cone conformer exhibits the requested ion selectivity. In case of thin membrane layers of calix(4)resorcinarene the common NMR and X-ray methods of structural analysis can not be used [3]. We chose FTIR and FT-Raman spectroscopy. IR spectral differences between cis-cis-cis and cis-cis-trans isomers were identified in the regions of ether group vibrations at 1170-1140 cm^{-1} and of out-of-plane C-H bonds vibrations at 830-860 cm^{-1}. Raman spectra exhibit even more clear differences in the regions of the ether vibration at 1230-1300 cm^{-1}, of the out-of-plane vibrations of the C-H bonds at 740-694 cm^{-1}, and of the skeletal vibrations at 420-440 cm^{-1}.

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SPECTROSCOPY AND STRUCTURE OF CH_3CH_2OCN AND CF_3CH_2OCN

P7.3

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Alkyl cyanates are known to isomerize easily into their thermodynamically more stable isocyanate derivatives. An interesting exception is CF_3CH_2OCN, which is stable at room temperature. Very little is known, however, about this molecule. The aim of this work was to characterize the electronic structure and geometry of CF_3CH_2OCN, as well as to find answer for its kinetic stability, in comparison with those of the unstable CH_3CH_2OCN. To this end *ab initio* and DFT calculations were done, and IR and photoelectron spectroscopic investigations were carried out. Of particular interest were the conformers of CF_3CH_2OCN and CH_3CH_2OCN, the isomerization process, and the electronic structure and vibrational spectra of both molecules. Table 1 shows the possible conformers of CF_3CH_2OCN and CH_3CH_2OCN calculated at the B3-LYP/6-311G(2d,2p) level.

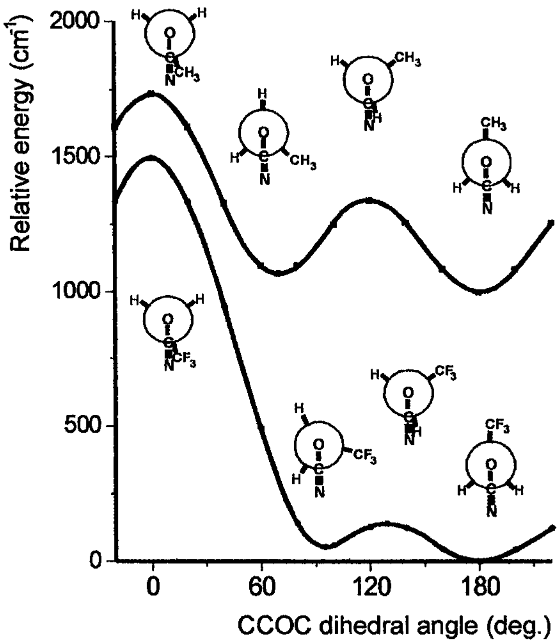

Figure 1 – Relative energies of the different conformers of CF_3CH_2OCN and CH_3CH_2OCN

P7.4

^{1}H NMR AND UV-Vis SPECTROSCOPY OF CHLORINE AND FLUORINE SUBSTITUTED STILBENES; CONFORMATIONAL STUDIES

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^{1}H NMR and UV-Vis spectroscopic studies as well as molecular mechanics calculations have been performed for the trans and cis isomers of a series of chlorine and fluorine substituted stilbenes. Correlations are found between predicted molecular conformations and various NMR and UV-Vis spectroscopic parameters, indicating that these are suitable for conformational studies. The ethylene proton chemical shifts, in particular, are found to be sensitive to anisotropy effects of nearby C-X (X=Cl,F) bonds. Both ethylene and some ring proton chemical shifts are found to be dependent on ring current effects, which are substituent and ring orientation dependent. UV spectra support the structural predictions based on the molecular mechanic vs. NMR correlation analysis. Average minimum energy conformations of compounds are given.

P7.5

CONFORMATIONAL STUDIES OF TWO BICYCLO[3.3.1]NONANE DERRIVATIVES BY MEANS OF VIBRATIONAL SPECTROSCOPY AND *ab initio* CALCULATIONS

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Vibrational spectra of newly synthesized derivatives of bicyclo[3.3.1]nonane – bicyclo[3.3.1]nonane-(2,6)-dione and bicyclo[3.3.1]-(2,9)-dione – were never studied and their conformational variety is unknown. Our quantum chemical *ab initio* calculations at HF level using 6-31G** basis set have shown that four conformers exist for bicyclo[3.3.1]nonane-(2,6)-dione and five conformers exist for bicyclo[3.3.1]-(2,9)-dione. Two low energy conformer of each title compound are presented in fig. 1. The calculations show that for bicyclo[3.3.1]nonane-(2,6)-dione the 'chair-chair' conformer is more stable than the 'chair-boat' conformer, whereas the opposite takes place in case of bicyclo[3.3.1]-(2,9)-dione.

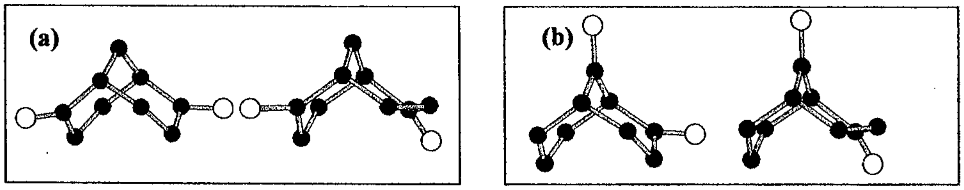

Fig. 1 - Low energy conformers of bicyclo[3.3.1]nonane-(2,6)-dione and bicyclo[3.3.1]-(2,9)-dione

IR absorption and Raman spectra of title compounds in gaseous, liquid and solid states as well in low temperature N_2 and Ar matrix were obtained. Raman spectrum of solid bicyclo[3.3.1]nonane-(2,6)-dione is presented in fig. 2.

By combining experimental and theoretical data complete assignment of the spectral bands will be presented. Distinction of experimental and calculated ΔH values will be discussed.

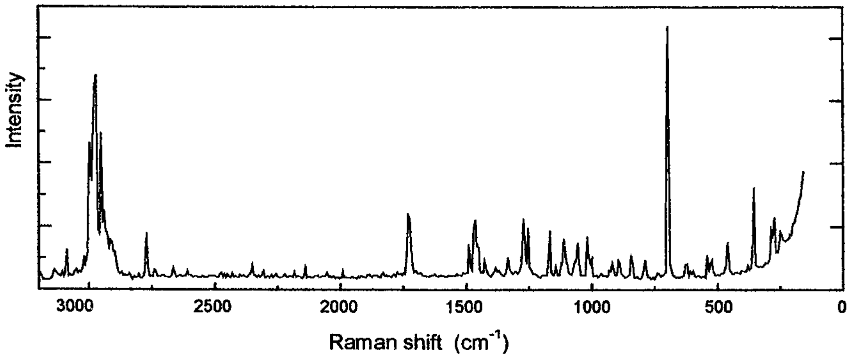

Fig.2 – Raman spectrum of solid bicyclo[3.3.1]nonane-(2,6)-dione

P7.6

INFRARED AND RAMAN SPECTRA, CONFORMATIONS AND *AB INITIO* CALCULATIONS OF CHLORMETHYLMETHYL DICHLOROSILANE

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The infrared spectra of chloromethylmethyl dichlorosilane ($ClCH_2CH_3SiCl_2$) were recorded in the vapour, amorphous and crystalline solid phases in the range 4000-50 cm^{-1}, and mid-IR spectra of the compound isolated in argon and nitrogen matrices at 5 K were obtained. Raman spectra of the liquid were recorded at various temperatures between 298 and 218 K in a capillary. The crystal was studied in the capillary at 210 K and spectra of the amorphous and annealed crystal deposited on a copper finger cooled with liquid nitrogen were recorded.

The spectra of chloromethylmethyl dichlorosilane showed the existence of two conformers - *anti* and *gauche* - present in the vapour and in the liquid. Approximately 5 Raman and 3 infrared bands, all weak, present in the fluid phases vanished upon crystallization. From three band pairs the enthalpy difference between the conformers were calculated in the liquid giving an average value ΔH(*anti-gauche*)=0.2±0.3 kJ mol^{-1}, suggesting *gauche* to be the low energy conformer. Similar data have previously been observed for other silanes with conformational equilibria[1-3]. In the argon and nitrogen matrices quite small intensity variations in the IR bands were observed after annealing to ca. 36 K (argon) or 30 K (nitrogen) suggesting negligible enthalpy difference also in the matrices.

Ab initio calculations were performed using the Gaussian 94 program with the HF/6-311G* basis function and gave optimized geometries, infrared and Raman intensities and scaled vibrational frequencies for the *anti* and *gauche* conformers. The conformational energy derived was 7.2 kJ mol^{-1}, *gauche* being the low energy conformer, while the *anti* conformer had a larger dipole moment than *gauche.* Correlation between the observed and calculated wavenumbers of both conformers revealed that *gauche* was present in the crystal, and assignments of the spectra have been carried out.

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INFRARED AND RAMAN SPECTRA, CONFORMATIONS AND *AB INITIO* CALCULATIONS OF DICHLORMETHYLMETHYL DICHLOROSILANE

P7.7

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The infrared spectra of dichloromethylmethyl dichlorosilane ($Cl_2CHCH_3SiCl_2$) were recorded in the vapour, amorphous and crystalline solid phases in the range 4000-50 cm^{-1}. Infrared spectra (4000-450 cm^{-1}) of the compound isolated in argon, nitrogen and krypton matrices were obtained at 5 K before and after annealing to temperatures in the range 15-50 K. Raman spectra of the liquid were recorded at various temperatures between 298 and 148 K in the range 3100-30 cm^{-1}. Spectra of the amorphous and annealed crystal deposited a copper finger were recorded. The spectra showed the existence of twoconformers - *anti* and *gauche* - in the vapour and in the liquid. Aproximately 6 infrared and Raman bands present in the fluid phases vanished upon crystallization. From intensity variations of two band pairs with temperature a ΔH^{O} value of 0.4 ± 0.3 kJ mol^{-1} between the conformers was obtained in the liquid, *anti* being the low energy conformer.

Negligible varations in the IR bands intensity were observed in each of the matrix spectra after annealing to 28 K (nitrogen), 33 K (argon) and 50 K (krypton). Apparently, the enthalpy difference between the conformers is very low in the matrices, as also observed for other silanes[1,2].

Ab initio calculations were performed using the Gaussian 94 program with the HF/6-311G* basis function and gave optimized geometries, infrared and Raman intensities and scaled vibrational frequencies for the *anti* and *gauche* conformers. The conformational energy derived was 4.4 kJ mol^{-1} with *anti* being the low energy conformer. The dipole moment was higher for *gauche* than the *anti* conformer. Correlation between the observed and calculated wavenumbers of both conformers revealed that *anti* was present in the crystal, and complete assignments of the spectra have been carried out.

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P7.8

CONFORMATIONAL ANALYSIS OF 3-CHLORO-TETRAHYDRO-1,3-OXAZINE

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The replacement of a β-methylene unit in the piperidine ring by a heteroatom (with its attendant lone pairs or substituents) has stimulated considerable interest in the study of the tetrahydro-1,3-oxazine, -1,3-diazine and –1,3-thiazine ring systems (Fig. 1). The large volume of experimental work produced allowed the understanding of the main features of their conformational analysis. However, past studies have been centered on the N-alkyl derivatives of these ring systems[1].

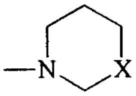

Fig. 1 – Tetrahydro-1,3-oxazine(X=O),-1,3-diazine(X=N-)and 1,3-thiazine(X=S)

We have extended our interests to N-heterosubstituted derivatives of the above mentioned ring systems and now we report the conformational analysis study of 3-chloro-tetrahydro-1,3-oxazine (Fig. 2), a flexible system in which both ring inversion and pyramidal nitrogen inversion can occur. Among the consequences of the presence of electron lone pairs on the atom directly bonded to the trivalent nitrogen is the significantly enhanced barrier to nitrogen inversion. From the introduction of the β-oxygen in the ring it is also expected an increase in the preference of the N-chloro group for the axial orientation.

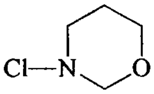

Fig. 2 – 3-Chloro-tetrahydro-1,3-oxazine

The compound under study, a novel derivative, was prepared by a modified literature method and its conformational analysis behaviour followed by ^{13}C DNMR. On lowering temperature the four sharp signals show broadening and resharpening as a consequence of the "slowing down" of a dynamic phenomenon that we assign to N-inversion. Activation and equilibrium parameters were determined by the "Anet Broadening Method"[2] and discussed in terms of previous related work.

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SPECTROSCOPIC STUDY OF 3-METHYL-AZABICYCLO[3.2.1]OCTAN-8α (AND β)-OLS.

P7.9

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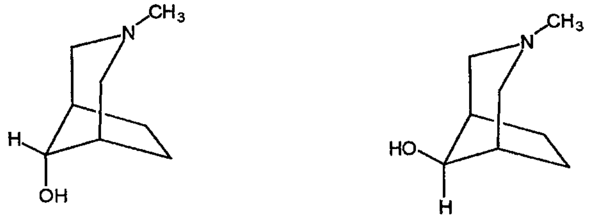
Previous paper (1,2) reported the synthesis, ^{1}H-NMR, ^{13}C NMR, IR studies and X-ray diffraction data for 3-phenethyl-3-azabicyclo[3.2.1]octan-8α(and β).ols.
In a research program devoted to the development of new pharmacological interesting compounds, we have synthetized 3-methyl-3-azabicyclo[3.2.1]octan-8α(and β)-ols. (scheme 1). The infrared and ^{1}H and ^{13}C NMR spectra of compounds I and II, have been examined in several media in order to establish the configuration of these interesting compounds.



I

II

Scheme 1

References:

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P7.10

VIBRATIONAL AND THEORETICAL DFT STUDY OF TWO REGIOREGULAR METHYL-DISUBSTITUTED BITHIOPHENES

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In this communication we report on the vibrational IR and Raman spectra of two β-alkyl substituted bithiophenes with well-defined substitution patterns: the 3,3′- and the 4,4′-dimethyl,2,2′-bithiophenes [1]. Interpretation of experimental data was aided by DFT calculations at the B3LYP/6-31G** level under the assumption of a C_{2h} molecular symmetry for both the systems. The satisfactory agreement between the experimental spectra and those of the planar model systems indicates that conformational distortions from coplanarity of the rings are not too large at room temperature. This means that π-conjugation between the two thiophene rings is the driving force which determines the minimum energy conformation of the molecular backbone. Geometry optimizations indicate that the nearly planar conformation in the head-to-head compound is achieved at the expense of large modifications in bond lengths and angles with respect to the tail-to-tail one, particularly for the C-S bonds.

The simplicity of the Raman spectra further supports the theoretical results. In this regard, the two bithiophenes show Raman features (i.e., the strong Raman activity of particular totally symmetric C=C stretching modes and the too few bands experimentally observed as compared with the number of Raman-active vibrations predicted by the optical selection rules) which are common to many other classes of oligothiophenes and that can be ascribed within the formalism of the Effective Conjugation Coordinate Theory to the existence of an efficient π-conjugation [2].

The DFT force field calculations have allowed us to perform a full vibrational assignment of the infrared and Raman spectra of the two compounds on the basis of the definition of a complete series of Pulay′s group coordinates [3], which should be useful for the interpretation of the spectra of longer oligomers.

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VIBRATIONAL ANALYSIS OF THE CONFORMATIONAL EQUILIBRIUM OF 3-FLUOROSTYRENE

P7.11

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Although the vibrational spectra of 3-Fluorostyrene were recorded many years ago, the first attempt to assign the different modes belonging to the *cis* and *trans* conformers (see Figure 1) was only made by Ribeiro-Claro et al. in 1993 [1]. These authors recorded the Infrared and Raman spectra, and assigned most of the vibrational wavenumbers by comparing them to those of similar molecules. In addition, they performed *ab initio* calculations at the HF/6-31G* level confirming the stability of the *cis* conformer in relation to the *trans* one. However, the nature of the optimized structures was not evaluated by computing the harmonic vibrational wavenumbers with the uncertainty that it implies.

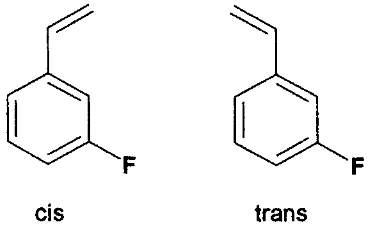

Fig.- Cis and Trans-3-Fluorostyrene

Therefore, the main aim of this work is to carry out a more accurate vibrational analysis for the 3-Fluorostyrene, supporting our assignments with *ab initio* and DFT calculations. Thus, the geometry and vibrational wavenumbers for the 3-Fluorostyrene have been calculated at the MP2 and B3LYP levels of theory, with different basis sets as 6-31G* and 6-311G**, for both *cis* and *trans* conformers. In addition, the Inelastic Neutron Scattering (INS) spectrum has been recorded for the first time and new Infrared and Raman spectra are also reported for this compound. One of the first steps in this analysis will be to check for the level of theory which, leading to a "good" minimum in the potential energy surface, best reproduces not only the vibrational data but also the INS features. This will be followed by refinement of the fitting to both wavenumbers and INS intensities starting from the force constants matrix calculated via *ab initio* or DFT.

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P7.12

THEORETICAL AND EXPERIMENTAL IR SPECTRA AND ASSIGNMENTS OF 3-AMINOPYRIDINE

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In our previous study [1] we have investigated the theoretical vibrational spectrum of free 2-aminopyridine and its some deuterated derivatives in valance force field approximation. In order to investigate the alterations of molecular parameters of pyridine, depending on position of the substituent, in this study we have calculated the vibrational spectra of free 3-aminopyridine. Approximate normal coordinate analysis is performed on the basis of different theoretical calculations. Quantum optimised (MNDO) geometry has been calculated by using GAMESS program [2] by taken into account the experimental geometry of 3-aminopyridine for the initial sets of parameters. For normal coordinate calculations with force field refinement method, program LEV [3] was used. For ab initio and semiempirical quantum calculations we have used program GAMESS [2]. The initial force field parameters of 3-aminopyridine were refined from the corresponding parameters of pyridine molecule. The results indicate that there are qualitative agreement between normal modes assignments, that are made upon quantum chemical calculations, force field refinement results and one made earlier upon experimental information.

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RAMAN AND INFRARED SPECTRA, CONFORMATIONAL STABILITY, NORMAL COORDINATE ANALYSIS, VIBRATIONAL ASSIGNMENT, AND *AB INITIO* CALCULATIONS OF *TRANS* 3-PENTENENITRILE AND 3-METHYL-3-BUTENE NITRILE

P7.13

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We previously investigated the conformational equilibria exhibited by allyl cyanide [1], 3-fluoropropene [2], and *trans*-1-fluoro-2-butene [3], where a methyl group replaced the hydrogen in the 1-position of 3-fluoropropene. The results of these studies showed that the three molecules exist as mixtures of *cis* and *gauche* conformers in the fluid phase. For allyl cyanide [1] and 3-fluoropropene [2], the *cis* conformer was found to be the more stable rotamer in the liquid phase and the only form remaining in the solid. However, the methyl derivatives of 3-fluoropropene enhanced the stability of the *gauche* conformer, causing it to be more stable than the *cis* form by 171±19 cm^{-1} in the liquid phase, as well as more stable in the solid phase [3]. In order to provide additional information on the effect of the methyl group in the *trans* position on the conformational equilibrium, we investigated the conformational stability of *trans*-3-pentenenitrile (*trans*-$CH_3CH=CHCH_2CN$).

The Raman (3200 to 20 cm^{-1}) spectra of liquid and solid *trans*-$CH_3CH=CHCH_2CN$, and the infrared (3200 to 30 cm^{-1}) spectra of gaseous and solid *trans*-3-pentenenitrile have been recorded. The spectra of the fluid phases are consistent with two stable conformers in equilibrium at ambient temperature. The mid-infrared spectra of the sample dissolved in liquid xenon as a function of temperature (-100 to -55°C) have been recorded. Utilizing two conformer pairs, the enthalpy difference has been determined to be 205±7 cm^{-1} (2.45±0.08 kJ/mol) with the *cis* conformer the more stable form. Vibrational assignments for the 33 normal modes for the *cis* conformer and several of those for the *gauche* form are proposed. Similar studies have also been carried out on 3-methyl-3-butene nitrile. The enthalpy difference has been determined to be 164±9 cm^{-1} (1.20±0.12 kJ/mol), with the *cis* conformer the more stable rotamer. These results will be discussed and compared to those obtained for some similar molecules.

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P7.14

STRUCTURE AND SPECTROSCOPY OF DISUBSTITUTED FUROXANS

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The disubstituted furoxans (1,2,5-oxadiazole 2-oxides, $X_2C_2N_2O_2$) with X = F-, Cl-, Br-, I-, H_3C-, NC-, and HC≡C- are investigated by calculations employing conventional *ab initio* methods and by density functional theory (DFT). In several cases (X = Cl-, Br-, H_3C- and NC-), the computational studies are supported by experiment in the form of geometric structures (X-ray diffraction), electronic structures (ultraviolet photoelectron spectroscopy) and vibrational spectroscopy (mid-infrared and Raman).

The spectroscopic and structural interest in these molecules lies in the fact that they are the ring dimers of the linear/quasi-linear nitrile oxide molecules, XCNO, which have recently been generated into the gas phase for the first time and investigated by a various spectroscopic methods [1-4]. Some of the furoxans investigated in this work provide thermolytic routes to these nitrile oxides, and conversely they pose loss routes (through dimerisation processes over low barriers) for the nitrile oxides. DFT calculations for the dimerisation mechanism of the nitrile oxides to the ring dimer furoxans have been investigated.

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VIBRATIONAL SPECTRA AND ASSIGNMENT OF PICOLINIC ACID AND ITS SODIUM SALT

P7.15

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The study of picolinic acid (2-Pyridinecarboxilic acid) is important from a biological, pharmaceutical, agricultural and chemical point of view. Thus, for instance, this molecule is the basis of several amphoteric ion exchange resins, herbicides (i.e. 3,6-dichloropicolinic acid or Clopyralid and 4-amino-3,5,6-trichloro-2-picolinic acid or Picloram) and reagents for qualitative and quantitative analysis[1].

As far as their vibrational spectra are concerned, there have been a number of incomplete assignments mainly focussed on the internal mode involving the COO(H) moiety , in order to demonstrate the being, or not, of intramolecular hydrogen bonding[2,3], as appears in figure 1.

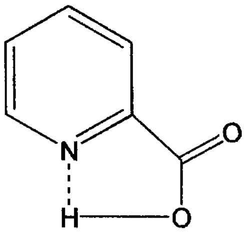

Figure 1. Intramolecular hydrogen bonding in picolinic acid.

This point is also dealt with in a study of the electron spectra[4] as well as an X-Ray diffraction analysis[5], where a sort of hydrogen bonding has to be admitted in the refinement procedure.

In this study, we have analyzed the vibrational spectra (IR and Raman) in different phases of picolinic acid and its sodium salt. Furthermore, in order to propose an assignment as complete as possible for both picolinic acid and its sodium salt, and to confirm the intramolecular hydrogen bonding, we have carried out *ab initio* (HF, MP2) and DFT/B3LYP levels, with 6-31G**, 6-311G** and 6-311++G** basis sets, and semiempirical (AM1 and PM3 levels) calculations.

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P7.16

SPECTROSCOPIC AND THEORETICAL STUDY OF CYCLOPENTADIENYL COMPLEXES

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Vibrational spectra of cyclopentadienyl (Cp) complexes have been widely studied. In spite of the great amount of experimental data, only a very few papers are available on the complete force constant calculations of these systems [1]. In the case of the pentamethylcyclopentadienyl (Cp*) compounds no experimental data and complete force field calculations are available up till now.

Infrared, far-infrared and FT-Raman spectra of $C_5(CH_3)_5Na$, $C_5(CH_3)_5Li$, $C_5H_5ReO_3$, $C_5(CH_3)_5ReO_3$, $C_5H_5Re(CO)_3$, $C(CH_3)_5Re(CO)_3$ and $C(CH_3)_5Mn(CO)_3$ molecules have been recorded both in solid and solution (THF, CH_2Cl_2) phases. Normal coordinate calculations (NCA) for all studied complexes and quantum chemical treatment by means of density functional theory (DFT) for alkali metal compounds were adopted for complete understanding of the vibrational spectra.

The influence of the ring substituents (CH_3 groups), of the oxidation state of the central atom (Re(I) and Re(VII)) and of the atom radius (Mn, Re) on the spectra, as well as on the M-C force constants will be discussed. Some of our results are listed in Table 1.

Table 1. Some representative stretching force constants (10^2 N m^{-1})

Force constant	$CpMn(CO)_3$	$CpRe(CO)_3$	$Cp^*Re(CO)_3$	$CpReO_3$	Cp^*ReO_3
K(C-C)	7,52	6,21	6,67	7,51	6,67
K(M-C)	3,43	4,03	6,11	3,66	3,81
K(M-CO)	2,80	3,62	3,86	-	-
K(ReO)	-	-	-	6,99	6,99
K(CO)	15,97	15,89	15,69	-	-

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^{1}H NMR STUDIES OF BETAINES, $\geq N^+-(CH_2)_nCOO^-$ (n=2,3) AND THEIR COMPLEXES WITH HYDROHALIDES

P7.17

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Betaine compounds, $\geq N^+-(CH_2)_nCOO^-$, are commonly zwitterions with two formally charged groups that are not conjugated. Betaines are found in complex lipids, in metabolic system and as transmethylating agents. The unique properties of betaines as amphoteric surfactants determine their usage in toiletries, care products, medicine, pharmacy, biology and other scientific applications.

In this contribution we analyze proton chemical shifts and coupling constants of alkylamino- and pyridine-betaines containing two or three methylene groups in the polimethylene bridging chain and their complexes with mineral acids. In all betaines with two CH_2 groups both N^+-CH_2 protons are magnetically equivalent, while in some betaines with three CH_2 groups they are nonequivalent. Some conclusion on conformations and electrostatic interactions between the charged groups will be presented.

P7.18

FT-IR AND MULTINUCLEAR NMR STUDIES OF TRIS(OXAALKYL) -BORATES AND -PHOSPHATES AND THEIR COMPLEXES WITH PROTON AND SOME METAL CATIONS

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Various inorganic esters of ethylene glycol were obtained [1]. FTIR and nuclear magnetic resonance of ^{1}H, ^{13}C, ^{11}B, ^{7}Li and ^{23}Na nuclei were used for the study of proton and metal cation complexation with tris(oxaalkyl)- borates and –phosphates [2]. We have demonstrated that ligands including three poly(oxaethylene) chains form proton or cation channels, in which large proton or metal cation polarizability due to the fast fluctuations of the cations is observed. In the FTIR spectra the fast fluctuation of the cation is indicated by continuous absorption. In the case of complexes with proton - it is observed in the middle IR region, whereas in the case of such cations as Li^+, Na^+ and K^+ - it is observed in the Far IR region. The dependence of the shape of the continua on the length of the channels, i. e. the number of minima in the multiminima potentials, demonstrates that the fluctuation of protons or metal cations occurs along the channel.

The NMR techniques have proved the formation of complexes and give the information about the character of the multiminima proton potentials in respective channels formed by three oxaalky chains [2, 3].

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P7.19

NMR SPECTROSCOPY STUDY OF THE PEROXOVANADIUM(V) COMPLEXES OF L-MALIC ACID

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Vanadate and peroxide have been shown to act synergistically to mimic insulin activity[1] and this mimetic ability has also been found for several peroxovanadium complexes.[2] These complexes are also known to have antitumor activity,[3] and have been studied as functional models for the vanadium haloperoxidase enzymes.[4] In addition to this biological relevance, a large variety of oxidation reactions can be efficiently performed by peroxovanadium(V) complexes.[1] In view of the interest on these compounds, in this communication we report on the peroxocomplexes of V(V) with L-malic acid, formed in aqueous solution.

By using multinuclear (^1H, ^{13}C and ^{51}V) NMR spectroscopy L-malic acid is found to form 13 peroxovanadium(V) complexes in the pH range 2-7. These complexes are monoperoxo species having VO^{3+} metal centers and a geometry close to pentagonal bipyramidal. The peroxo group is bound in the equatorial plane relative to the apical oxo terminal group (V=O) and the remaining apical and equatorial positions are occupied by the carboxylic and the hydroxyl groups of the ligand. A similar study has been carried out on the peroxovanadium(V) complexes of L-lactic[5] and glycolic[6] acids.

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P7.20

VIBRATIONAL, ^{1}H NMR AND MÖSSBAUER SPECTROSCOPIC CHARACTERIZATION OF INDOLE-3-ACETIC ACID COMPLEXATION WITH IRON

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Indole-3-acetic acid (IAA), a phytohormone of the auxin series, is of essential biological significance. Being widely distributed in higher plants, IAA is also well documented to be synthesized by a number of soil microorganisms which excrete it into the environment. As a result, plant growth regulation is thus induced via the influence of IAA on plant root growth and development.

As a chemically active substance, IAA excreted into soil in noticeable quantities can also interact with certain soil components including metal cations, influencing their chemical and biological availability. Iron, one of biologically essential metals, is usually abundant in soil largely in the form of ferric hydroxo compounds, yet being of extremely low bioavailability owing to their negligible solubility. It has been shown that IAA as well as some of its metabolically related precursors including anthranilic acid and L-tryptophan [1-4] are capable of reductive solubilization of iron(III) under certain conditions, which is of certain ecological significance.

Iron(III) complex with IAA was obtained and some of its physicochemical properties and structural characteristics were studied using Fourier transform infrared (FTIR) and FT-Raman, ^{1}H NMR and ^{57}Fe Mössbauer spectroscopic techniques. Whereas the Mössbauer data featured the state of the iron cation in the complex, special attention was also paid to the state of certain functional groups (side chain carboxyl, indole N–H), responsible for metal binding, both in IAA and in its complex with iron(III), as derived from the vibrational spectroscopic and ^{1}H NMR data. The latter were obtained in deuterated acetone solution, as the iron(III) complex had been found to be well soluble in oxygen-containing organic solvents (ethanol, acetone, diethyl ether), in contrast to, e.g. CCl_4 and water. While in weakly acidic aqueous solutions iron(III) is gradually reduced by IAA, which was followed using Mössbauer measurements, in circumneutral media the Fe^{III} complex is relatively stable.

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URANIUM(IV)-POLYOXOMETALATES COMPLEXES WITH P(V), Si(IV), Ge(IV), As(III), Bi(III), Sb(III) AS HETEROATOMS: SPECTROSCOPIC INVESTIGATION (IR, UV-VIS, ESR)

P7.21

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The lacunary polyoxometalates (POM) are intensely studied for their ability to stocking the radioactive waste. The following sandwich-type uranium(IV)-polyoxometalates: $Na_n[(UO)_3(H_2O)_6(ZW_9O_{34})_2]\cdot xH_2O$ (**1**: Z = P, n = 12, x = 21; **2**: Z = Si, n = 14, x = 0; **3**: Z = Ge, n = 14, x = 0) and $Na_n[U_3(ZW_9O_{33})_2]\cdot xH_2O$ (**4**: Z = As, n = 6, x = 15; **5**: Z = Bi, n = 6, x = 18; **6**: Z = Sb, n = 6, x = 0) were prepared and investigated by FTIR, UV-VIS and ESR spectroscopy.

The uranium(IV) coordination at the trilacunary Keggin units change the positions and shape of the $\nu_{as}(W\text{–}O_{b,c}\text{–}W)$, $\nu_{as}(W{=}O_d)$, $\nu_{as}(W\text{–}O_a)$ antisymmetric stretching vibration bands in the 750–950 cm^{-1}regions of all U(IV)-complexes FTIR spectra. The symmetry of the ZO_4 central units seems to increase after U(IV) coordination in the complex with P, but decreases in the others.

The visible electronic absorption spectra of U(IV)–POM complexes, performed in aqueous solutions, correspond to the $^3H_4$ electronic ground state into a quasicubic configuration [1]. The sharp L band ($^3H_4 \rightarrow {}^3P_0$) is centered at 14100÷15000 cm^{-1}, the O band ($^3H_4 \rightarrow {}^1D_2({}^1G_4)$) at 15000÷16250 cm^{-1} in all spectra and the other bands appear as shoulders (R: $^3H_4 \rightarrow {}^3P_1$ at 17450÷17800 cm^{-1} except for **2**; V: $^3H_4 \rightarrow {}^1I_6$ at 19600÷20800 cm^{-1}; W: $^3H_4 \rightarrow {}^3P_2$ at 22500÷24900 cm^{-1} except for **1** and **4**). The U(IV)–W(VI) charge transfer band begins at ≈ 25000 cm^{-1}. The UV electronic spectra of the U(IV)–POM complexes and of the ligand in aqueous solution presents two broad bands assigned to: $p_\pi\text{–}d_\pi$ electronic transitions into the W=O bonds (at 46000÷47300 cm^{-1} for the ligands and the most shifted for antimony(III) (+640 cm^{-1}) and bismuth (–560 cm^{-1}) complexes) and $p_\pi\text{–}d_\pi$ transitions into tricentric W–O–W bonds (at 40800÷41600 cm^{-1} for the ligand and 38800÷40800 cm^{-1} for the uranium complexes).

The uranium(IV)-polyoxometalates with germanium, arsenic and bismuth presents in the ESR spectra one (the first complexes) or two signals (the last) with some features, centered at $g \approx 2.0$. These correspond to a Γ_5 ground state with $S_{ef} = 1$ effective spin for U(IV) in quasicubic environment.

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P7.22

SPECTROSCOPIC STUDIES OF SOME OXYGEN-BONDED COPPER(II) β-DIKETONATES COMPLEXES

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Current interest in metal β-diketonates arises from their application as contact shift reagents for better resolution of the nuclear magnetic resonance spectra of a variety of complex organic molecules, in laser technology and in the polymer industry.

The β-diketonates copper(II) complexes $Cu(L1)_2$, $Cu(L2)_2$, $Cu(L3)_2$, where L1 = $H_3C{-}CO{-}CH_2{-}CO{-}CH_3$, L2 = $H_5C_6{-}CO{-}CH_2{-}CO{-}C_6H_5$, L3 = $H_5C_6{-}CO{-}CH_2{-}CO{-}OC_2H_5$, were prepared and investigated by spectroscopic (FTIR, UV-VIS, EPR) methods. These spectroscopic techniques provide valuable information regarding the nature of the carbonyl group attached to the Cu(II) ions and also about the quasi-aromatic behavior of the six-membered chelate ring and the structural features of metal β-diketonate derivatives [1].

The coordination of the Cu(II) ion at the oxygen atoms of two β-diketonates molecules is observed by the shift of the $\nu_s(C=C)$, $\nu_s(C=O)$ and $\nu_{as}(C=O)$ stretching vibrations in the complex spectra comparative to the ligands spectra [2]. While the L1 ligand presents only a broad band centered at 1613 (vs,b) for these vibrations, the $Cu(L1)_2$ has three vibrations (1523 s,sp; 1547 s,sp; 1592 m,sp). In the $Cu(L3)_2$ complex these vibrations are red shifted with $\approx 40\ cm^{-1}$.

In the visible electronic spectra of the Cu(II)-β-diketonates complexes the electronic d-d transitions are obtained. The very broad absorption band of $B_{1g} \rightarrow B_{2g}$ transition appears at $\approx 15370\ cm^{-1}$ for $Cu(L1)_2$, $\approx 13910\ cm^{-1}$ for $Cu(L2)_2$ and $\approx 14970\ cm^{-1}$ for $Cu(L3)_2$. The spectrum of $Cu(L1)_2$ complex also presents a shoulder at $\approx 10967\ cm^{-1}$ attributed.

The powder ESR spectrum of $Cu(L1)_2$ complex is axial ($g_{\parallel} = 2.216$, $g_{\perp} = 2.050$) and typical for square-planar compounds. The EPR spectrum of $Cu(L2)_2$ is rhombic, with $g_1 = 2.163$, $g_2 = 2.144$ and $g_3 = 2.071$, and that of $Cu(L3)_2$ complex is quasiisotropic and asymmetric ($g_0 = 2.084$). These low gyromagnetic factors arise also from the delocalization of the unpaired electron in the chelate rings and some molecular packing effects.

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MULTINUCLEAR NMR STUDY OF THE COMPLEXATION OF D-GULONIC ACID WITH OXOIONS OF Mo(VI) AND W(VI)

P7.23

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Following our previous studies on the complexation of sugar acids with oxoions of Mo(VI) and W(VI), using multinuclear NMR spectroscopy,[1] in this communication we report on the complexes formed in aqueous solution of M(VI)/D-gulonic acid (M=Mo, W).

By using multinuclear (^{1}H, ^{13}C, ^{17}O, ^{95}Mo, ^{183}W) magnetic resonance spectroscopy (1D and 2D), D-gulonic acid is found to form 7 and 10 complexes, respectively, with molybdenum(VI) and tungsten(VI), in aqueous solution, depending on pH and metal:ligand molar ratios. Two isomeric 1:2 (metal:ligand) complexes involving the carboxylate and the adjacent OH group are present in the pH range 2-9. At intermediate and high pH, molybdate forms a tetradentate 2:1 complex involving the four secondary hydroxyl groups of the ligand, whereas tungstate forms one 2:1 tridentate species. At low and intermediate pH values, three 2:1 complexes are found for both metals, involving the carboxylate group and three secondary hydroxyl groups, and a 5:2 species involving the carboxylate group and all the secondary hydroxyl groups; tungstate can also form two additional n:m (n>m) species, involving, respectively, all and the secondary hydroxyl groups, besides the carboxylate group. In alkaline solutions tungstate is able to form an additional 2:1 pentadentate complex involving all the hydroxyl groups of the ligand.

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P7.24

EXPERIMENTAL AND THEORETICAL STUDY OF THE IR SPECTRA OF PARAPHENYLENEDIAMINE TRANSITION METAL (II) COMPLEXES

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Paraphenylenediamine (1,4-diaminobenzene) (PPD), a well-known electron donor in CT complexes, has attracted substantial attention in the studies of photochemical processes. In our previous study [1] we have investigated the vibrational spectrum of free paraphenylenediamine, in both cis and trans conformations. We now investigate the effect of coordination of PPD to a transition metal. The aim of this work is theoretical analysis of the normal vibrations for coordinated PPD in comparison to the experimental results. Our main interest is to investigate the IR spectrum and coupling peculiarities of the metal-ligand vibrational modes of coordinated PPD. The NH_2 vibrational modes of PPD are found to be much affected on complex formation. For example whilst the values of the NH_2 stretching and NH_2 bending modes were found at lower values than the corresponding ones in the free molecule, the NH_2 twisting and NH_2 wagging modes were found at higher values in all the PPD complexes. The alterations were explained by means of the changes in hybridisation about the nitrogen atoms on coordination. In order to check the coordination effects on the PPD ligand we have calculated the vibrational wavenumbers and IR intensities of the coordinated molecule by the aid of the force field and electrooptical parameters of the free ligand. The reliable force field and electro-optical parameters of coordinated PPD have been determined by refinement in order to fit the experimental wavenumbers and intensities of transition metal (II) PPD complexes. For theoretical calculations, program LEV [2] was used. Calculated spectra have been compared with the experimental spectra of previously reported $MCl_2(PPD)$ (where M= Ni or Cd) [3] and new $CdI_2(PPD)$ and $MnCl_2(PPD)$ complexes. The resultant force field is checked by the deuteration process. In this study the complete vibrational the assignments of the IR wavenumbers of the $CdI_2(PPD)$ and $MnCl_2(PPD)$ complexes were made by the aid of normal coordinate analysis of coordinated PPD.

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EXPERIMENTAL AND THEORETICAL SPECTROSCOPIC INVESTIGATIONS OF 4-CHLOROPYRIDINE AND ITS TRANSITION METAL COMPLEXES

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In our previous studies the experimental results of the vibrational spectroscopic studies of chloropyridine (Clpy) transition metal(II) tetracyanonickelate complexes were reported [1-3]. It was shown that several modes of Clpy had upward shifts in frequency when compared with those of free molecule and the shifts were metal dependent. Now we make an attempt of theoretical investigation of coupling peculiarities of the metal-ligand vibrational modes of 4-chloropyridine (4Clpy). Normal coordinate analysis is carried out on the infrared and Raman spectral data of 4Clpy and its deuterated analogs to determine a reliable valance force field of the free ligand. The aim of this study is to calculate the adequate parameter sets for 4Clpy which has a primary importance for our study of coordinated 4Clpy, and then investigate the coordination effects on 4Clpy ligand. On the other hand, we have prepared 2 new compounds of the form $M(4Clpy)(NH_3)Ni(CN)_4$ (M = Mn or Co) and the assignments of the IR spectra are made depending on the theoretical calculations. The results indicate that M atom is bounded from the nitrogen atoms of ammonia and 4Clpy molecules. A partially common and well transferable force field has been obtained for the free 4Clpy and in the first step, this force field was introduced in calculating the IR spectrum of coordinated 4Clpy. Later the force field was refined in order to obtain the experimental IR spectra of the transition metal (II) 4Clpy complexes.

For theoretical calculations, program LEV [4] was used. Since experimental geometry of 4Clpy is not known, quantum optimised geometry has been used in the spectral calculations. After refinement procedure the differences between experimental and theoretical wavenumbers were found to be less than ± 10 cm^{-1} for most of the vibrations. The calculated molecular parameters of 4Clpy have been compared to those of 2-chloropyridine and 3-Chloropyridine [3,5] and found that certain vibrational modes of pyridine affected much depending on the position of the substituent. In this study coordination effect on the 4Clpy modes are also discussed.

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P7.26

VIBRATIONAL STUDY OF LITHIUM, SODIUM, POTASSIUM, RUBIDIUM AND CESIUM NICOTINATES

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In our earlier works the influence of various metals and halogens on the electronic structure of the benzoic and salicylic [1] acids have been studied. Those ligands have been treated as models to study enzymes and other biologically important molecules.

The aim of this paper has been to synthesise complexes of lithium, sodium, potassium, rubidium and caesium with nicotinic acid, to register and assign their vibrational (FT-IR, and FT-Raman) spectra and to compare the electronic charge distribution in molecules of studied compounds. The nicotinic acid is very interesting model, as it is a biologically important ligand incorporated into some enzymes and which molecules are an active agent in some drugs.

Our spectral assignment has been based on the literature data [2] and previous theoretical studies [3]. The bands which occurred in the spectra were divided into two groups: (i) those connected with carboxylic anion vibrations and (ii) those connected with aromatic ring vibrations. In the first group characteristic wide and intense bands responsible for the asymmetric (ν_{asym}: 15651 - 1537 cm^{-1}) and symmetric (ν_{sym}: 1499-1386 cm^{-1}) stretching of the carboxylic anion were observed. Furthermore bands assigned to the symmetric (β_{sym}: 865 – 845 cm^{-1}) and asymmetric (β_{asym}: 542 – 528 cm^{-1}) deformations in plane of the carboxylic anion as well as symmetric (γ_{sym}: 747 – 766 cm^{-1}) deformations out of plane of the carboxylic anion were present. The bands connected with aromatic ring vibrations (the second group) were observed in the whole spectral range (4000 – 400 cm^{-1}). The observed changes in wavenumber of carboxylic anion bands in the series Li→Na→K→Rb→Cs were small, but characteristic. The wavenumber of the ν_{sym} and β_{sym} decrease, γ_{sym} increase, while ν_{asym} and β_{asym} do not change systematically in this series. The wavenumbers of the aromatic bands 19a and 19b slightly decrease and wavenumbers of the other aromatic bands do not change systematically. The conclusion is, that metal influences the vibrational structure of the whole molecule (carboxylic anion and aromatic ring), and electronic charge distribution depends on metal properties most strongly on its ionic potential.

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VIBRATIONAL STUDY OF ALKALINE METAL NICOTINATES, BENZOATES, p-HALOGENBENZOATES AND SALICYLATES

P7.27

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The studies have been undertaken to estimate electronic charge distribution in the aromatic ring of benzoic, salicylic or nicotinic acids in relation to their complexes with different metals [1 - 4]. These compounds act as models of biologically important compounds, e.g. enzymes. Using vibrational and UV absorption spectroscopy it was previously shown that heavy metals, such as Hg (I), Hg (II), Ag and Pb (II) as well as alkaline metals disturb the aromatic system of benzoic and salicylic acids [2 –3]. A meaningful decrease in both frequency and intensity of selected aromatic bands occurs for IR and Raman spectra of metal complexes in comparison with these of uncomplexed ligands. Within the UV range hipsochromic shift of bands responsible for $\pi \rightarrow \pi^*$ transition are observed.

The aim of present work is to study and compare (by FT – Raman, FT – IR, UV absorption spectroscopy and X –ray methods):

(a) the influence of Li, Na, K, Rb and Cs on the aromatic system of benzoic, *p*-halogenbenzoic, salicylic and nicotinic acids,
(b) the effect of halogens on the electronic system of complexes of *p*-halogenbenzoic acids,
(c) the effect of mass and halogens.

Distinct changes of spectra occurred in the following regions : about 1610 – 1450 cm^{-1} [$\nu(CC)_{ar}$], 1360 – 1000 cm^{-1} [$\beta(CH)$], and 970 – 740 cm^{-1} [$\gamma(CH)$]. In the paper we present a correlation between observed changes of the wavenumbers of these bands and the ionic potential as well as electronegativity of central ion for investigated complexes.

The effect of investigated metals on different ligands (benzoic, salicylic and nicotinic acids) have been compared. The ionic potentials and electronegativities of halogens and metals are main factors responsible for perturbation of electronic charge distribution in the ring in case of all ligands.

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P7.28

LANTHANIDE IONS COMPLEXATION BY URONIC ACIDS

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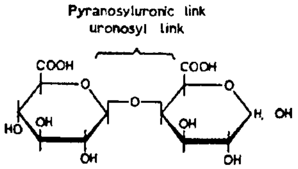
In view of the growing industrial and commercial use of toxic metals (e.g. actinides, lead, mercury, cadmium or arsenic) and their increasing release into the atmosphere, the problem of developing effective treatments for such exposure will undergo a growing importance in the future. Simultaneously, such events as Chernobyl fallout have shown the importance of the studies leading to the development of new therapeutic methods for the removal of immobilized heavy and/or radioactive metals.

Numerous clinical tests have shown that several natural polysaccharides, e.g. alginic acid (a straight chain, polyuronic acid comprised of anhydro α-D-mannuronic acid and L-guluronic acid) or pectines (partially methoxylated polygalacturonic acid), used as prophylactic or medication drugs in the case of heavy and radioactive metal poisoning induce their increased excretion.



On the other hand, similarity in the ionic radii of the trivalent lanthanides with those of *calcium* and *sodium*, in the charge density (Z/r) with *magnesium* or *zinc* provides the possibility of their mutual isomorphous replacement. In connection with unique magnetic and spectroscopic properties, the REEs are informative substitution probes in the various biological and medical examinations. Simultaneously, because of their chemical similarity, REEs may also act as substitution probes for the actinides - radioactive elements applied both in nuclear industry and weapons[1].

So, the purpose of present work, as a part of more general program of analysis of metal-sugar acid complexes, is to examine the interaction between D-glucuronic and D(+)-galacturonic acids and the trivalent REE cations. Complete study of these complexes has not been made until now, and the results reported by different authors are conflicting even in the compound composition[2]. FT-IR and Raman spectra of the crystalline D(+)-galacturonic and D-glucuronic acids, as well as their lanthanum salts have been recorded, assigned and discussed in terms of the structure of the investigated complexes.

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EFFECT OF SODIUM(I), CALCIUM(II), LANTHANUM(III) AND THORIUM(IV) ON THE AROMATIC SYSTEM OF p-HYDROXYBENZOATES

P7.29

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The objective of present work, as a part of more general program of analysis of metal interaction with various substituted benzoic acids [1-4], is to examine electronic charge distribution in the aromatic ring of *p*-hydroxybenzoic acid with these for the complexes with different cations. The compounds mentioned above act as models of biologically important compounds, e.g. enzymes.

The series of investigated cations, Na(I), Ca(II), La(III) and Th(IV), consists of the species of similar radii but different charges.

Interaction of the investigated metals with the aromatic system of *p*-hydroxybenzoic acid has been studied by molecular spectroscopy techniques: two vibrational methods (FT-IR and FT-Raman), as well as by the UV absorption spectroscopy.

It has been found, that distinct changes of vibrational spectra occurred mainly in the following areas:

- 1610 – 1450 cm^{-1}, where both the wavenumbers and intensities of several bands related to the skeletal vibrations of the aromatic ring, $\nu(CC)_{ar}$, change monotonically along the Na(I) → Th(IV) series,
- 1580 – 1380 cm^{-1}, where the asymmetric and symmetric bands of the carboxylic anion have appeared [$\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively],
- 800 – 650 cm^{-1}, bands assigned as the deformation of the C-H bonds, $\gamma(CH)$.

It has been found that variation of the ionic potentials along the investigated metal series, of their electronegativities and of their weights are equally the factors responsible for the differences in the electronic charge distribution in the aromatic ring of the *p*-hydroxybenzoic acid.

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P7.30

THE INFLUENCE OF SELECTED METALS (Mg, Ca, Sr AND Ba) ON THE ELECTRONIC SYSTEM OF THE p-HALOGENBENZOIC ACIDS

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In our previous works [1-2] the influence of alkaline metals on the aromatic system of benzoic and salicylic acids was studied. The wavenumber, and intensity of the bands occurring in the spectra were analysed. It was estimated that potassium (among studied metals) and iodine (among studied halogens) disturb aromatic system in the highest degree. The increase of the ionic potential of the metal or halogen brought about the decrease in uniform charge distribution in the ring. In the case of halogens the ionic potential was even more important than polarity of C-X bond.

The aim of this work is to study the influence of both ions of the metal of second group of periodic table, and halogens on the electronic system of p-halogenbenzoic acid complexes. Furthermore, the comparison of the influence of mono (earlier works) and bivalent ions is to be done. The arising question is if in the case of bivalent metal complexes, in which the ratio metal/ligand is 1:2 (elementary analysis) and the structure of the carboxylic anion (quantum calculations) differs from the monovalent metal complexes, the same parameters of metal and halogen play main role in the changes of the charge distribution in the whole molecule. In view of the main chemical and physical properties of the chemical compound depending on the electronic charge distribution in the whole molecule, spectral changes are especially interesting.

The assignment of the spectra of p-halogenobenzoic acid complexes with magnesium, calcium, strontium and barium have been proposed. The influence of mentioned metals on the electronic system of p-halogenbenzoic acids have been under study. The biggest differences in wavenumber of selected bands depending on metal ion occurred within the spectral range: 1540-1520 cm^{-1}, 1145-1130 cm^{-1}, and 870-850 cm^{-1}. On the other hand the influence of halogen (F, Cl, Br, I) on the electronic system of complexes was investigated. The effect of halogen was mostly seen within the spectral range: 1610-1570 cm^{-1}, 1510-1495 cm^{-1}, 1180-165 cm^{-1}, 1025-1005 cm^{-1}, 865-850 cm^{-1}, and 690-675 cm^{-1}. Main parameter responsible for the changes in the vibrational structure of the molecules was the ionic potential.

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THE EFFECT OF SELECTED METALS ON THE ELECTRONIC SYSTEM OF BIOLOGICALLY IMPORTANT LIGANDS

P7.31

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In our earlier papers it has been found that heavy and alkaline metals perturb the uniform electronic charge distribution in the aromatic ring of benzoic an salicylic acids [1-2]. This effect occures in vibrational spectra: the wavenumber and intensity of some aromatic bands decreased comparing to these of free ligands. In the UV range the hipsohromic shift of the $\pi \rightarrow \pi^*$ band has been observed, and the NMR data show that the ring current intensity decreases. Finally, the semi-empirical calculations indicate an increase in dipol moment of the whole molecule, increase in bonds polarity and decrease in delocalisation energy.

The aim of this paper is to study the influence of metal (Li, Na, K, La, Nd, Dy and Lu) and halogen (F, Cl, Br and I) on the vibrational structure of metal complexes with p-halogenobenzoic acids. Benzoic acid and its derivatives are taken as model systems representing a wide group of aromatic ligands which are incorporated into enzymes.

Systematic decrease in wavenumber of the bands 19a, 10a, 8a, 8b, 6a and 4 (notation given in literature [3]) along with the series $F \rightarrow Cl \rightarrow Br \rightarrow I$ was observed. The decrease in the wavenumber of the bands was correlated linearly with the decrease in the ionic potential of the halogens. Similar effects were observed for the entire metal series, and relationship between ionic potential of the metal and wavenumber of the bands occurred as well. In the studied compounds the increase in the ionic potential of the halogen causes an increase in the difference between wavenumber of $\nu_{asym}COO^-$ and $\nu_{sym}COO^-$, contrary to an increase in the ionic potential of the studied metals. Among halogens the ionic potential is lowest for iodine and this substituent brings about maximal nearer of the symmetric and asymmetric bands of the carboxylic anion. On the other hand sodium broaden those bands in the highest degree (amoung studied metals). Both opposite effects are seen in the case of sodium p-iodobenzoate.

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P7.32

STRUCTURAL AND VIBRATIONAL CHARACTERIZATION OF METHYL α-HYDROXY-ISOBUTYRATE IN THE GLASSY STATE, LIQUID PHASE AND ISOLATED IN AN ARGON MATRIX

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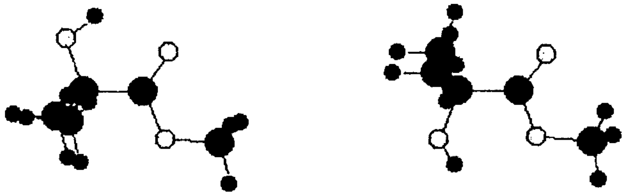
Methyl α-hydroxy-isobutyrate (**MHib**), as other α-hydroxy substituted carboxylic compounds, has drawn the attention of many people due to its important medical and pharmaceutical applications [1,4].

In this study we used vibrational spectroscopy (both Raman and infrared) to shed light on the nature of the different phases exhibited by **MHib**, and quantum chemical calculations to help interpretation of the vibrational data.

It was found that in the glassy state as well as in the liquid phase and isolated in an argon matrix **Mhib** exists in two conformational states. The C_s point group *Syn-Syn* conformer (**Ss**), which exhibits an intramolecular OH···O= hydrogen bond, was found to correspond to the most stable form. The relative population of the second more stable conformer, *Gauche-Skew* (**GSk**), increases in the liquid phase, since intermolecular interactions tend to reduce the importance of the intramolecular H-bonding that is the main stabilizing factor of the **Ss** form.

These results follow closely the previous data obtained for methyl glycolate [5].



Most stable conformers of **MHib**

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A VIBRATIONAL SPECTROSCOPIC STUDY OF R-1-AMINO-2-PROPANOL

P7.33

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Simple aminoalcohols are very interesting compounds which present suitable physicochemical properties to act as cryoprotectants [1]. Recently, we started a systematic study of aminoalcohols with two and three carbon atoms in order to obtain spectroscopic and thermodynamic properties of these compounds, at different temperatures and states, as well as to understand the role played by the H-bonding interactions in determining these properties.

The simultaneous presence of the OH and NH_2 groups in aminoalcohols allows the establishment of different types of intra- and intermolecular hydrogen bonding. The intramolecular H-bonding can be of two types: OH...N and NH...O, the former being considerably stronger than the later. These interactions are responsible for the stabilisation of certain conformations in the different physical states.

Following the methodology previously used to study 2-amino-1-etanol [2], 3-amino-1-propanol [3] and 2-amino-1-propanol [4], we present now recent results obtained for 1-amino-2-propanol.

The isolated molecule was studied by matrix isolation infrared spectroscopy in Ar and Kr matrices. With the help of *ab initio* calculations, carried out at the HF and MP2 levels of theory, it was possible to characterise the most stable conformations assumed by the monomers and to assign the matrix spectra. The calculations were also used to interpret the spectroscopic results (infrared and Raman) obtained for the pure liquid.

A comparison between the results obtained for 1-amino-2-propanol and those previously reported for other aminoalcohols is presented. The relative strengths of the different intramolecular H-bonding in the various molecules, in different states, are also reported and interpreted.

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Spectroscopy and Chemical Dynamics (1)

-Hydrogen Bonding
-Solvation Dynamics
-Solvent Effects

THE HYDROGEN-BOND EFFECTS ON MOLECULAR PROPERTIES OF *TRANS*-AZOBENZENE IN ACIDIC SOLUTIONS

P8.1

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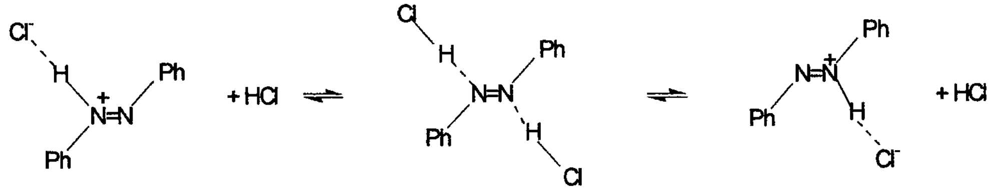
The protonation of *trans*-azobenzene, tAB, in an acidic solution has been studied by ^{13}C NMR [1] and vibrational Raman [2] spectra and DFT calculations. In the ^{13}C NMR spectra, on the one hand, there is only one signal for the C-1,1' atoms which is more shielded than in neutral solutions. In the Raman spectra, on the other hand, only the bands assigned to the azo-group are characterized by significant broadening. These results suggest that there should be intermolecular interactions, such as hydrogen bonds, which lead to the fast proton two-site exchange between acid molecules and azo-nitrogens. The structural and spectral parameters as well as interaction energies for the hydrogen - bonded complexes involved in the following equilibria between tAB and hydrochloric acid have been studied in the gas phase by the DFT B3LYP method using various basis sets:



The bulk solvent (ethanol, water) effects on energies of complexes have also been determined with the self-consistent reaction field model.

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P8.2

HYDROGEN BONDING INTERACTIONS IN SOME BENZOPYRANOPYRIDINE ESTERS

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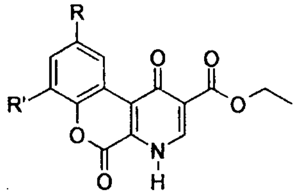
Weak interatomic interactions, such as hydrogen bonds, play a dominant role in many chemical and biochemical processes. Hydrogen bonds in four different molecules of benzopyranopyridine esters (Fig.1), which exert their antibacterial activity by inhibiting DNA gyrase [1-3], have been investigated by means of NMR and IR spectroscopy and quantum chemical calculations. All NMR spectra were recorded in DMSO-d_6 solution while IR spectra were recorded in DMSO solution and solid state. Quantum chemical calculations were performed at the semi-empirical level using PM3 Hamiltonian. Significant changes in vibrational frequencies, NMR chemical shifts and calculations have pointed toward the formation of different interactions in solid state and solution. In compound **2** the observed tautomeric equilibrium is slow on the NMR time scale and is governed by strong intramolecular hydrogen bonds.



Compound	R	R'
1	H	H
2	$NHCOCH_3$	H
3	H	F
4	NO_2	H

Fig.1 - Benzopyranopyridine esters

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HYDROGEN BONDING BEHAVIOUR OF LINEAR OLIGOPEPTIDES WITH A FLUORINATED ALCOHOL

P8.3

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It is general knowledge that linear peptides exhibit a random or extended conformation in solution if no functions are introduced into the molecules which inhibit the flexibility of the peptide backbone. Lately it was found that also tripeptide derivatives dissolved in apolar solvents form intramolecular hydrogen bonds in a C_7 arrangemen[1]. In continuation of this work we have investigated protected di- and tripeptide derivatives with apolar side groups (e.g. Ala, Val, Phe) by means of FTIR spectroscopy. The asymmetric band profile of the amide I signal indicates the existence of preferred conformers in the peptide backbone in methylene chloride solutions. The corresponding region of the CH_2Cl_2, DMSO, D_2O and HFiP solutions will be compared. Supported by band deconvolution and peak fitting techniques an assignment of these conformers will be attempted. Additionally the results of CD measurements will be presented.

Furthermore, the association behaviour of the oligopeptide derivatives dissolved in CH_2Cl_2 with HFiP (1.1.1.3.3.3-hexafluoropropan-2-ol) will be discussed. It was found that the alcohol interacts with the urethane protecting groups of the oligopeptide and the peptide bond. On the other hand the ester carbonyl function is not involved in hydrogen bonding. In order to understand the association behaviour ^1H NMR titration of the peptide solutions with HFiP was performed. On the hand of the shift of the NH signals the centres of the HFiP association can be assigned. For dipeptide derivatives Z-Ala-Ala-OMe (Z= benzoyloxycarbonyl,) the alcohol associates preferably with the peptide function and changes the shielding properties of the urethane function. For Z-Ala-Ala-Ala-OMe the association behaviour of both peptide functions is different.

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P8.4

EFFECT OF INTRAMOLECULAR HYDROGEN BONDING ON THE PREDICTABILITY OF QSAR DESCRIPTORS

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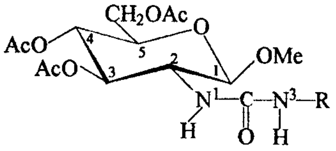
On the search for effective anticancer drugs with similar structure as streptozotocin but less side effects a number of amino acid and dipeptide analogue derivatives were synthesised and their acetylated species sketched in Fig. 1 were characterised with respect to their hydrophobic and solvation properties.



Ac= acetyl
R= amino acid or dipetidyl ester

Fig. 1 General structure of the ureido sugar amino acid/dipeptidyl esters

Therefore, a comprehensive HPLC study was performed and the data were analysed using multiple regression analysis of HPLC data in order to receive descriptors characterising the ability of the molecules to interact in certain partitioning systems based on the solvation equation by Abraham[1]. These descriptors are the excess molar refraction R_2, the dipolarity/polarisability π_2^H, the effective hydrogen bond basicity $\Sigma\beta_2^H$, the effective hydrogen bond acidity $\Sigma\alpha_2^H$ and the McGowan volume V_x. The comparison of the experimental descriptors with values calculated from fragmental descriptors give a good correlation for V_x, R_2 and π_2^H whereas strong deviations were observed for $\Sigma\beta_2^H$ in the cases of Gly, D-Val, Phe-Gly and Ala-Phe in the side chain.

Besides HPLC data the results of FTIR and ^1H NMR investigations on these systems will be shown in order to understand the intramolecular hydrogen bonding. Obviously, steric properties and the chirality of the amino acid residues influence the equilibrium constant and the association enthalpy of the formed C_7 and C_5 intramolecular hydrogen bonds.

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SPECTROSCOPIC STUDIES OF N-METHYLMORPHOLINE BETAINE WITH PHENOLS

P8.5

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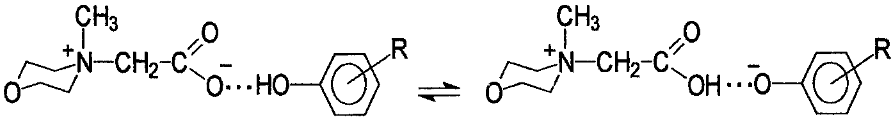
N-methylmorpholine betaine, as a good proton-acceptor, forms crystalline complexes with substituted phenols (in a large range of their proton-donor properties). The complexes have been studied by UV-VIS, ^{1}H and ^{13}C NMR in solution and by FTIR in a solid state. Complexes with hydrogen bond can exist in a prototropic equilibrium as a molecular complex (**1**) or an ion-pair (**2**).



1 **2**

This prototropic equilibrium strongly depends on the proton-donor properties of phenols, as well as the polarity of the solvent used (DMSO, CH_3CN, CH_2Cl_2). FTIR spectra show a broad absorption in the 1500-400 cm^{-1} region. Its centre of gravity shifts to lower wavenumbres when proton-donor properties increased. ^{1}H and ^{13}C NMR can also be used to recognize the molecular complex or ion-pair species. Correlations between some spectroscopic data and pK_a of phenols will be discussed.

P8.6

$[OHO]^-$ AND $^+[NHO]^-$ HYDROGEN BONDS IN THE 2:1 ADDUCT OF PENTACHLOROPHENOL WITH 7-METHYL-1,5,7-TRIAZABICYCLO[4.4.0] DEC-5-ENE $[(PCP)_2 \cdot MTBD]$

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The results of X-ray diffraction and IR spectroscopic studies for 2:1 pentachlorophenol-7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene $[(PCP)_2 \cdot MTBD]$ adduct are reported. The short asymmetric $[OHO]^-$ hydrogen bonds of 2.508(2) Å are formed showing broad IR absorption with two maxima located at ~1200 and ~2400 cm^{-1}. The second maximum is interpreted as the 0–>2 transition between split levels in asymmetric double minimum potential. One of the oxygen atoms forms an additional $O \cdots H\text{-}N^+$ hydrogen bonding with a MTBD cation. The situation is somewhat different in the acetonitrile solution whose IR spectrum shows continuous absorption extended over whole of the IR region. In acetonitrile the dissociation to the free OHO^- and ^+NH ions takes place and the OHO^- bridges become dynamically symmetric. The broadening is interpreted as due to stochastic distribution of the geometry and Zundel polarizability. The geometry of MTBD cations reflects equal distribution of the positive charge among three nitrogen atoms.

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STRUCTURE, PHASE TRANSITION AND INFRARED SPECTRA OF 1,2-CYCLOHEXANEDIOL

P8.7

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Calorimetric studies performed on 1,2-cyclohexanediol isomers and published in previous work [1] pointed out remarkable differences between *cis* isomer and the *trans* enantiomeric form. For instance, whilst for the *trans* enantiomers only one stable crystalline phase is present, for *cis* isomer the lower temperature crystalline phase is transformed into a plastic crystal before melting.

Since hydrogen bonding plays a determinant role in the molecular interaction in these substances infrared spectroscopy can provide a deep insight into the structure. Thus, the aim of this paper is to use this technique in order to understand structural differences between those isomers and the phase transitions occurring by heating or cooling these substances.

Powder FTIR spectra for *cis*-1,2-cyclohexanediol and for the two *trans*-1,2-cyclohexanediol enantiomers were recorded for different temperatures during heating-cooling cycles in the temperature range from 20°C to the melting point of the substances under consideration. The study to be presented is based on the stretching vibration mode of the OH groups. To provide support for the deconvolution of the absorption band a statistical test was applied to the spectroscopic data. Band resolution was viewed as a model building problem based on parsimony test.

The experimental F_{exp} value is calculated according to

$$F_{exp} = \frac{(SS_{(f)} - SS_{(f+1)})/\Delta p}{\chi^2_{(f+1)}}$$

where f is the number of peaks considered into the model, Δp the number of questionable parameters. F_{exp} is compared with critical value $F_{1-\alpha(\Delta p, n-p)}$. Superfluous number of parameters can be excluded when $F_{exp} \leq F_{1-\alpha(\Delta p, n-p)}$.

The application of this statistical test leads to five peak functions for *cis* isomer while the parsimonious model for *trans* contains six peak functions.

Molecular modeling studies based on the crystallographic data quoted in literature for the substances under study were carried as an attempt for ascribe hydrogen bonding peak functions to structural features.

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P8.8

NEUTRON SPECTRSCOPY AND *AB INITIO* STUDY OF HYDROGEN BOND DYNAMICS IN L - SERINE AND L - THREONINE

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The structures and molecular dynamics of aliphatic amino acids, which constitute the building blocks of protein systems have been for many years the subject of rising interest and importance and hence, the subject of intensive studies. Crystallographic data indicate that L-serine and L-threonine occurs in the solid state in the dipolar ion (zwitterion) form and the amino and hydroxyl group hydrogen atoms participate in a network of strong hydrogen bonds. It has been shown that the spectroscopy of incoherently scattered neutrons (IINS) offers significant advantages in the study of molecular motions in crystals. Since hydrogen nuclei exhibit particularly large cross section for the incoherent scattering of thermal neutrons, internal modes in which hydrogen atoms participate produce IINS spectra of much higher intensity than other modes. Moreover, the substitution of hydrogen by deuterium (whose incoherent scattering cross section is almost 40 times smaller while the oscillator mass is twice as large) permits the identification of modes due to hydrogen vibrations in the molecule. We have measured IINS spectra of the samples of normal and deuterated L-serine and L-threonine. In the latter, only amino and hydroxyl group hydrogen atoms were substituted by deuterium. In addition, all samples were examined by Raman and IR spectroscopy. IINS frequencies due to the out-of plane γ(N-H...O) and γ(O-H...O) hydrogen bond motions were observed and identified. The results of the present experiment provide valuable additional information to the results obtained earlier in the course of IR and Raman spectroscopy studies. A comparison of IINS spectra recorded for the normal and deuterated samples of the same compound uniquely identyfies the modes due to vibrations of hydrogen atoms participating in the hydrogen bond network. As in the case of many other amino acids, IINS has proved to be an effective tool for investigating the dynamics of hydrogen bonds in their crystals.

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P8.9

$O_2(a^1\Delta_g)$ ABSORPTION AND $O_2(b^1\Sigma_g^+)$ EMISSION IN SOLUTION: QUANTIFYING THE a-b STOKES SHIFT

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The effect of solvent on the radiative transitions of dissolved oxygen is a problem of long-standing interest.[1] We have recently shown that $O_2(a^1\Delta_g)$ absorption, $a^1\Delta_g \rightarrow b^1\Sigma_g^+$, and $O_2(b^1\Sigma_g^+)$ emission, $b^1\Sigma_g^+ \rightarrow a^1\Delta_g$, can be monitored at ~5200 cm^{-1} in a number of different solvents using nanosecond time-resolved infrared spectroscopy.[2] In the present study we set out to examine the extent to which the a-b Stokes shift, recorded as the difference between the absorption and emission maxima, is solvent dependent.

The maxima of both absorption and emission spectra depend significantly on the solvent, indicating significant solvent dependence of the $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ energy levels. The corresponding Stokes shifts, however, are small, less than 5 cm^{-1}, as shown in Fig. 1 for the case of CCl_4. This indicates that the difference between the equilibrium and nonequilibrium solvation energies for the $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ states is small. Within our error limits, it is difficult to ascertain whether the Stokes shifts are solvent dependent. It is nonetheless clear that since the Stokes shifts are very small, any solvent-dependent change in the Stokes shift will likewise be small.

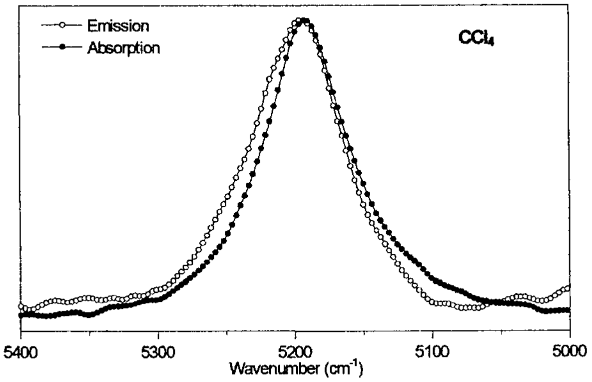

Fig. 1 - b→a Emission and a→b absorption spectra of O_2 recorded in CCl_4

The data were also modelled using *ab initio* computational methods, and these results indicate that both long- and short-range interactions between oxygen and the perturbing solvent must be considered to adequately describe spectroscopic transitions in dissolved oxygen.

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P8.10

CHAIN-LENGTH DEPENDENCE OF THE HYDRATION PROPERTIES OF SATURATED PHOSPHATIDYLCHOLINES AS REVEALED BY FTIR SPECTROSCOPY

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Lipids, and in particular phospholipids, are - in terms of their occurrence as important biomembrane constituents - an interesting class of molecules. They exhibit remarkable polymorphism, and water content is a major factor for regulating it. Apparently, hydration effects are biologically relevant since they are critical in the delicate interplay of the weak forces and interactions that determine, on balance, which phase eventually exists under the conditions given in a lipid system [1,2].

Recently, Fourier-transform infrared (FTIR) spectroscopy well known as a powerful physicochemical method in lipid research for a long time [3] has been successfully applied to reveal hydration-induced phenomena in some unsaturated phosphatidylcholines (PCs; these are the lipids most abundant in eukaryotes), in particular the existence of isothermal lyotropic phase transitions at room temperature (RT) [4]. Here, we present data obtained by studying films of a series of symmetric saturated diacyl PCs, with chain lengths n of 10, 12, 14, 16, 18 and 22, at RT in terms of water activity which was varied *via* ambient relative humidity (RH).

IR spectroscopy enables not only to monitor structural/conformational/phase changes arising in lipid molecules and aggregates due to the binding of water, but also to generate adsorption isotherms. The latter is realized by plotting a magnitude for the relative (normalized by the absorbance of C-H stretches) absorbance of the strong O-H stretching-vibration band of water near 3400 cm^{-1}, A_{wr}, versus RH. After correcting A_{wr} values for n, the capacity of the studied lipids to imbibe water can be directly compared. In fact, water uptake steadily decreases with growing n.

Short-chain lipids with $n \leq 14$ undergo lyotropic main transitions whereas the other PCs maintained a rigid phase at any RH. The lower n the smaller is the water activity necessary to trigger chain melting in the short-chain PCs.

The process of water binding could be followed, on a submolecular scale, by analysing relevant IR-absorption band parameters (wavenumbers, band widths) in terms of A_{wr}. The picture emerging for the different lipids is discussed in special regard to their phosphate and carbonyl moieties.

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INTERPRETATION OF THE ISOTOPE EFFECT ON SOLUBILITY OF METHANE IN WATER BY USING SPECTROSCOPIC DATA

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The differences in the solubility between isotopically substituted methanes in water will be interpreted in terms of the statistical theory of isotope effects in condensed systems by using spectroscopic data of the vapor and solution phases. The calculations require information on the frequencies of the hindered translational and rotational motions of the methane molecules in the aqueous phase and the shifts of the internal vibrational frequencies of the methane molecule on its transfer from the vapor into the aqueous phase.

The solubility of deuteromethane (CD_4) in liquid water was determined between 10 and 50 ^oC using a high-precision apparatus and compared with that of CH_4 available in the literature. The results display an inverse isotope effect, i.e. CH_4 is more soluble in water than CD_4 (e.g. at 25 ^oC by 1.5%). On the other hand the $^{12}C/^{13}C$ isotope effect is normal, i.e. the solubility of $^{13}CH_4$ is higher than that of $^{12}CH_4$ (e.g. at 20 ^oC by 0.06% [1]).

The frequencies of the IR active asymmetric vibrations of methane molecules in the aqueous phase were determined in the saturated solution of methane in heavy water using a Bio-Rad FTS-175 FT-IR spectrometer, equipped with an MCT detector, in a 0.2 mm CaF_2 cell. The hindered translational and rotational frequencies of methane in liquid water were obtained from a molecular dynamics study of the methane water system [2].

The results of the model calculations indicate that the $^{12}C/^{13}C$ solubility isotope effect is determined by the hindered translational motions of methane molecules in the aqueous solution and by the vapor - aqueous phase shifts of the asymmetric vibrations of the methane molecule. In the case of the H/D isotope effect there are also significant contributions from the hindered rotations of methane molecules in the aqueous phase, shifts of the symmetric vibrations and the non-classical rotation of the methane molecule in the vapor phase.

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P8.12

QENS STUDY OF HYDRATION EFFECTS ON TREHALOSE AQUEOUS SOLUTIONS

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Among disaccharides, trehalose, a naturally-occurring glass-forming disaccharide, is particularly effective in terms of its ability to preserve and maintain activity and leavening capacity of several desiccation-resistant organisms[1,2]. Even if different models [3-5] have been proposed to explain how trehalose exerts its protective action, at present a comprehensive answer is still lacking. We collected data using the NEAT spectrometer at the Berlin Neutron Scattering Center (BENSC) on α,α-trehalose deuterated samples in D_2O and on α,α-trehalose hydrogenated samples in H_2O at different water content. The employment of H/D substitution allows the separation of the diffusive dynamics of water from that of trehalose. The aim of the work is to furnish new results on the molecular dynamics of trehalose and to investigate the effect of this disaccharide on the neighboring water. This study is part of a comprehensive research effort to understand the molecular processes underlying the bio-protectant effectiveness of the disaccharide using a plenty of physical techniques (Light scattering, Nuclear Magnetic Resonance (NMR), Neutron scattering, thermodynamic measurements). The data analysis furnishes a microscopic whole-molecule diffusion coefficient in good agreement with NMR results and gives evidence of internal dynamics of trehalose. Furthermore it results that the dynamics of the neighboring water is strongly affected by the presence of trehalose. This finding could be related to the hypothesis [6] that the crystallization process in presence of trehalose is obstructed by a reduction of the amount of freezable water.

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NONLINEAR BEHAVIOR ON SOLVATION DYNAMICS STUDIED BY RISM THEORY: A PREDICTION FOR SPECTROSCOPIC EXPERIMENTS

P8.13

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We have applied a reference interaction-site model (RISM) theory to estimate the dynamic response function of the average-energy relaxation of the solute-solvent system, *S*(*t*). In various polar solvents we calculate *S*(*t*) induced by an instantaneous change of the solute electronic distribution (from the neutral to charged states). *S*(*t*) shows an obvious nonlinearity, which can be ascribed to the density fluctuation of the solvent.

We have studied solvation dynamics by means of parallel approaches of both experiments [1] and theory [2]. From an experimental side, solvation dynamics has been conventionally detected by using the time-resolved fluorescence (TRF) or transient hole-burning (THB) spectroscopy. *S*(*t*) can be determined on the basis of the first moment of the TRF or THB spectral function, $\nu(t)$:

$$S(t) = \{ \nu(t) - \nu(\infty) \} / \{ \nu(0) - \nu(\infty) \}$$

In this study we employ the RISM theory in connection with the site-site Smoluchowski-Vlasov equation in order to predict *S*(*t*). The theoretical descriptions used in this framework have been previously reported by Hirata and coworkers. [2]

For solutes, we first investigate a simple ion: (Cl -> $\mathrm{Cl}^{\delta-}$), then we study dipoles, quadrupoles, and octapoles. In their final states δ+ / δ- like charges are located on each site, separated by 6 Å. We make a stepwise change for δ starting from 0.0 to 0.2, 0.5, 0.75, and finally up to 1.0, for the ion and multipoles.

In the case of the ion solute the vast majority (>99%) of *S*(*t*) decays within 1 ps, where the decay curves of *S*(*t*) are absolutely fit by a single exponential and do not show any δ-dependence. The slow decays ranging from 1 ps to tens of ps regions are observed even though their contribution to the total-energy relaxation is very small (<1%), which show on the other hand highly non-exponential components and remarkable δ-dependence. For multipoles, the fast parts of *S*(*t*)s' decays also show δ-dependence, which were not able to be fit even though by using three-component exponential curves. Furthermore when the solute is getting large, or the value of δ is increased, *S*(*t*) becomes extremely slow.

We can attribute the δ-dependent aspects of *S*(*t*)s to the nonlinear response of the solvent dynamics, because *S*(*t*) itself is a scaled, said alternately, normalized quantity. At the present stage of our investigation, we suggest that the physical origin of the nonlinear *S*(*t*)s may be assigned to the solvent-density fluctuation. We now perform further theoretical approaches to elucidate the molecular origin of the nonlinearity, for instance, by means of the calculation of time-dependent radial distribution functions of solvent-sites viewed from solutes. We emphasize that the present theoretical results can be an important predication when one chooses solutes for experiments on solvation dynamics. As experimentalists, we will actually carry out some experiments to reproduce the results, which have been implied by the present RISM theory.

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P8.14

SOLVENT EFFECTS ON THE VIBRONIC STRUCTURE OF $S_1 \leftarrow S_0$ TRANSITION OF RHODAMINE 3B

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The spectral bandshape of an electronic transition is determined by the molecular orbital symmetry as well as by the amount of charge transferred. The vibronic structure reflects the vibrational sublevels through Franck-Condon factors. Spectra of homocyclic (e.g. benzene, pyrene or fullerenes[1]) and heterocyclic compounds (e.g. porphyrins) can thus provide information on the molecular environment.

In this contribution we report on the study of the $S_1 \leftarrow S_0$ steady absorption spectra of the ionic chromophore 9-(2-ethoxycarbonyl)phenyl-3,6-bis(diethylamino)-xanthylium (Rhodamine 3B), in water, n-alcohols (n=6 and 10), polyols (1,2-ethanediol and glycerol), glycerol triacetate and also in 1-chloro-naphthalene, where its (perchlorate) ion associated form is found. The spectral bands are resolved into three Gaussian components, which can be assigned to the 2←0, 1←0 and 0←0 vibronic contributions[2,3].

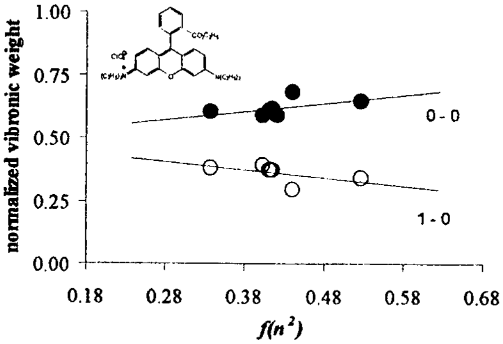

Figure 1 – Rhodamine 3B 0←0 and 1←0 vibronic contributions.

The weight of the 1←0 vibronic, decreases with increasing optical refractive index, while the opposite occurs with the 0←0 contribution. Both variations are linearly correlated with Onsager's reaction field function $f(n^2)$ (see Figure 1). This difference will be discussed in terms of variations in the nature and strengths of the couplings involved. In media of low (1-hexanol) and high (glycerol) static dielectric permittivity the ratios of the vibronic contributions are temperature independent[3], providing further evidence of the dominant effect of the electronic polarization.

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THE BIREFRINGENCE FROM CHANNELED SPECTRA OF POLY(PHENYL METHACRYLIC) ESTER OF CETYLOXYBENZOIC ACID SOLUTION IN TETRACHLOROMETHANE IN AN EXTERNAL ALTERNATE ELECTRIC FIELD

P8.15

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The anisotropic properties of poly(phenyl methacrylic) ester of cethyloxybenzoic acid (PPMAECOBA) in a thermodynamically "poor" solvent
such as tetrachloromethane (TCM) are explained by dipolar orientation of the polymer side chains [1]. The PPMAECOBA in TCM becomes a nematic polymer liquid crystal.

The birefringence of the PPMAECOBA in TCM solution has been determined both from channeled spectra [2] and with a polarising microscope with a compensatory wedge [3]. The experiments were made in an external alternate electric field with variable frequency. The channeled spectra were recorded using a double beam spectrophotometer and a device consisting in an anisotrope solution between two crossed polarisers [4].

A decrease of the birefringence with the increase of the frequency of the alternate external field applied to the cell containing the anisitrope solution was found. That proves the hyphothesis that the order from this solution is made up by the orientation of dipolar side chains of the macromolecules.

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P8.16

CONCENTRATION DEPENDENCE OF ν(C-Br) BAND SHAPE OF 2-BROMOPROPANE IN DIFFERENT SOLVENTS

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The parameters of ν(C-Br) vibrational mode of 2-bromopropane, observed at 537.4 cm $^{-1}$ in infrared spectrum of neat liquid, are influenced by non-specific interactions with solvents [1].

A study concerning the effects of dilution of 2-bromopropane in solvents of different polarities may give information about the interactions in the vicinity of C-Br bond. The linear band center shift upon dilution and an additional line width, with a maximum at a concentration of about 0.5 mole fraction, in 2-bromopropane with acetonitrile mixture have been evidenced. This behavior could be explained in terms of concentration fluctuations around the solute molecule.

In non-polar solvents like hexane, carbon tetrachloride or carbon disulfide, the increasing of band maximum frequency on dilution has been observed. The deviation from linearity is correlated with a local and bulk different composition of the mixture. The local microscopic mole fraction was estimated.

The number of solvent molecules in the interaction volume, N, is an important variable in the model developed by Knapp and Fischer [2] to describe concentration dependence of the vibrational band shape in binary mixtures. As in this model a Lorentzian band shape in neat liquid and dilute solutions is assumed, while for 2-bromopropane an important Gaussian contribution has been evidenced, a value of 4 to 6 for N, in solvents like hexane and carbon tetrachloride, is only an approximation. In the studied solvents only those molecules of the first coordination shell, which are in the vicinity of bromine atom, influence the ν(C-Br) vibrational mode2-bromopropane.

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SOLVENT EFFECTS IN INFRARED SPECTRA AND *AB INITIO* CALCULATIONS OF 2- BROMOPROPANE

P8.17

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Vibrational frequency shifts and intensity changes were observed in infrared spectra of 2-bromopropane, on going from the gas phase to solutions in polar solvents. No specific interactions with the solvent were detected. A detailed study of ν(C - Br) vibrational mode showed that, excepting aromatic hydrocarbons and chloroform, a linear dependence of the peak maximum on the dielectric function $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ is observed [1].

The effect of the solvents on the vibrational frequencies was examined theoretically via the Onsager reaction field. In this model, the solute is placed in a spherical cavity immersed in the solvent which is taken as an unstructured dielectric continuum, characterized by the dielectric constant ε. Calculations have been performed by using the GAMESS package of programmes [2] within the framework of RHF *ab initio* method, with various basis sets (3-21G, 6-31G, 6-311G, DZV, SBK-ECP).

The effects of the cavity radius and of dielectric properties of medium on the optimized geometry and on the calculated vibrational frequencies of 2- bromopropane are analysed. For ν(C - Br) band the experimental frequency shift from the gas phase to dilute solutions is well reproduced by the shift of calculated frequencies using the 631-G basis set, a cavity radius of 3.9 Å and values of dielectric constant between 2 and 36.

Ab initio infrared frequencies of 2-bromopropane calculated at HF and MP2 level are compared with the measured values for gas phase sample. The scaling of calculated harmonic frequencies by factors recommended in literature it's not the best method to obtain a better agreement with experimental values. An extended basis set for bromine atom may be a solution.

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P8.18

THE IMINO-AMINO TAUTOMERIC EQUILIBRIUM IN CYANOGUANIDINE DISSOLVED IN SEVERAL APROTIC SOLVENTS. AN FT-RAMAN SPECTROSCOPIC STUDY

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Cyanoguanidine (dicyandiamide) is an interesting molecule from either biological and chemical points of view, whose solid state structure has raised several theoretical as well as experimental controversies. It has been suggested(1) that the structural peculiarities observed in the lengths of the different C–N bonds (excluding the nitrile group), whose very similar bond distances are between those coresponding to the single and the double bond, could be explained assuming the coexistence of both the imino and amino tautomeric forms of the compound. Although in the solid state the predominant form should correspond to the imino tautomer, which is predicted to be more stable according to theoretical studies(2-4), the dissolution of cyanoguanidine in appropriate solvents could reveal the presence of both tautomers in equilibrium.

In this study, the FT-Raman spectra of cyanoguanidine solutions in *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and hexamethylfosforic triamide (HMPA), in a range of concentrations between $R = 3$ and $R = 10$ (R = solvent/solute mole ratio), are studied in detail. The cyanoguanidine vibrational bands studied here are the $\nu(C\equiv N)$ mode at 2100-2250 cm^{-1} and the $\nu_s(NCN)$ mode at 923 cm^{-1}. The intense doublet which appears in the spectral region of the nitrile stretching fundamental is attributed to the presence of the tautomeric imino (2147 cm^{-1}) and amino (2186 cm^{-1}) forms. Furthermore, in both bands a shoulder is evident in the higher frequency wings which could arise from cyanoguanidine molecules associated through hydrogen bonds affecting the nitrogen atom of the nitrile group. When the solute concentration is increased, the relative intensity of that band arising from the imino tautomer raises and a further increase in concentration of the associated species can be also observed. These observations are common to the three solvents studied. The concentration of the imino form strongly depends of the solvent, increasing in the order DMF < DMSO < HMPA which qualitatively corresponds with the donor number ranking. The presence of associated species, however, seems to be controlled by the dielectric constant of the solvent being minimal in DMSO, moderate in DMF and most important in HMPA

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INFLUENCE OF THE SOLVENT POLARITY ON THE PHOTOPHYSICAL PROPERTIES OF NORHARMAN

P8.19

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Norharman (Figure 1) presents interesting photophysical properties and has been proposed as a fluorescence standard [1]. These properties are strongly influenced by the solvent. In previous works, [2, 3] the photophysic of Norharmane in organic solvents such as: dichloromethane, dioxane, bencene, acetonitrile with different amounts of acetic acid was studied. The emission of the four species shown in Figure 1 can be detected and the ratio between them depends on the solvent, acetic acid ratio and excitation wavelength.

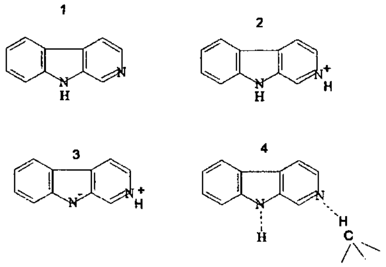

Fig. 1- Chemical structures of Norharman in excited state. 1, neutral form; 2.cationic form, 3, zwitterionic form, 4 phototautomer (detected in dichloromethane)

There are some open questions as for example, the origin of zwitterionic form. It is still not clear if it is formed from the cationic or from the neutral form. To gain insight in the knowledge of the photophisical properties of Norharman and to complete previous works, the steady-state and time-resolved fluorescence studies of Norharman in solvents with different dielectric constant (mixtures of bencene, dioxane and acetonitrile with acetic acid) has been carried out. The quantum yield of the neutral and cationic forms has been calculated and the decay time of the different foms have been determined.

From this study, it can be concluded that the higher the dielectric constant, the lower the quantum yield of the neutral form. And, as for the origin of the zwitterionic form, the rise time of the biexponential fitting of the decays curves exciting neutral form and registering the emission of the zwitterionic form in dioxane and bencene, seems to show that the neutral form give rise to the zwitterionic form.

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P8.20

FT-RAMAN STUDY OF LITHIUM AND SILVER TRIFLATE SOLUTIONS IN ACRYLONITRILE / *N,N*-DIMETHYLFORMAMIDE MIXED SOLVENT

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In this work, which continues our series on solvation and ionic association in acrylonitrile (ACN) solutions(1-4), different solutions of lithium or silver trifluoromethanesulfonate (triflate) in a mixed solvent formed by ACN and *N,N*-dimethylformamide (DMF) are studied by FT-Raman spectroscopy. In these, the mole fraction of the salt is kept constant (mole fraction, χ_{SALT} = 0.09), changing the solvent composition from samples rich in acrylonitrile (χ_{ACN} = 0.81) to nearly equimolar samples (χ_{ACN} = 0.44; χ_{DMF} = 0.48). The composition of the solvation sphere in both ions is calculated through the study of the modifications induced by the presence of the salt in the nitrile C≡N stretching at 2228 cm^{-1} and in the NC antisymmetric stretching of DMF at 658 cm^{-1}. The degree of ionic association is evaluated through studying the components of the triflate anion SO symmetric stretching band at 1032 cm^{-1}.

As could be expected taking into account the donor numbers of ACN and DMF, the latter preferentially solvates both cations. The preference is less pronounced in the case of Ag^+ which tends to interact strongly with nitriles(5), although it is very remarkable that Li^+ is solvated exclusively by DMF molecules in the equimolar mixed solvent. The total average solvation number remains virtually constant in Ag^+ (n = 3.5±0.1) and is augmented in Li^+ when the molar fraction of DMF increases. This observation arises as a direct consequence of the degree of ionic association.

Lithium triflate is considerably associated in those samples rich in ACN, where the predominant species (69.2%) seem to be the ionic aggregates (ν_{SO} = 1050 cm^{-1}) in the χ_{ACN} = 0.81 sample. However, the situation changes completely in the equimolar samples, with a high concentration (64.5%) of spectroscopically free anions (ν_{SO} = 1032 cm^{-1}). These findings are easily explained considering the corresponding dielectric constants of both co-solvents and their different donating ability. In silver triflate solutions, the degree of ionic association is low and remains approximately constant despite the changes in the

2–FORMYLPYRIDINETHIOSEMICARBAZONE AND ITS METHYL DERIVATIVES: SPECTROSCOPIC STUDIES ON THEIR BEHAVIOURS IN DIFFERENT SOLVENTS AND WITH IONS

P8.21

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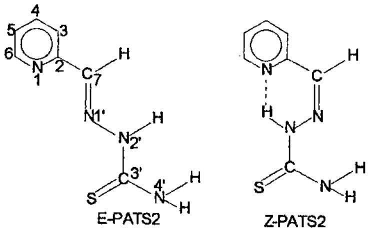
The chemistry of the 2-formylpyridinethiosemicarbazone (PATS2) family has been studied extensively, in part because of its pharmacological properties [1] but also because of its ability to be chemically adsorbed on gold electrode enhancing redox reactions of certain cytochrome c molecules [2]. These two properties are extremely dependent on the configuration (anti (E) and syn (Z)) of these compounds [3], Figure 1.

Figure 1. Schematic structure of E and Z-PATS2.



The Z-E isomerization of PATS2, 2-formylpyridine-2'-methyl thiosemicarbazone (2MePATS2), 2-formylpyridine - 4' -methyl thiosemicarbazone (4MePATS2) and 2-formylpyridine - 4', 4' - dimethyl thiosemicarbazone (DMePATS2) was studied in various solvents by Raman and NMR spectroscopies. The interactions of alkali and alkaline earth perchlorate salts with these compounds were also investigated in acetonitrile (Acn) solution.

The results showed that the most favourable configuration in the solid state is E for PATS2 changing to Z configuration when methyl groups substitute the two hydrogen atoms of the N (4') thiourea. In solution the E-Z equilibrium is affected by the solvent employed (H_2O, DMSO, Acn and CH_2Cl_2) making possible to change the E/Z relation for PATS2 and DMePATS2. These results are rationalised considering that the open structure (E) is preferential in solvents where solvent-compound hydrogen bonding interaction is possible. The ClO_4^- is a catalyst for the E to Z isomerization of PATS2 in Acn but has no effect in the isomerization of DMePATS2. The spectroscopic results also show that only DMePATS2 forms complexes with Na^+, Li^+, Mg^{2+}, Ba^{2+} and Ca^{2+} in Acn.

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P8.22

FROM HALOGEN-ETHYLENES TO LEWISITE: STRUCTURAL DYNAMIC MODELS, ELECTRONIC STRUCTURE, VIBRATIONAL SPECTRA

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Detailed analysis of vibrational spectra of halogen-ethylenes and comparison of solutions for inverse spectral problems for these compounds showed that extensive theoretical experiment has considerable drawbacks. One of them is unsatisfactory correspondence to such structural dynamic parameter as bond length – bond order. There are also some discrepancy in the values of electro-optical parameters for the whole set of compounds. We consider that these drawbacks arise from the attempt to solve a mechanical vibrational problem using only harmonic approximation of vibrational theory, ignoring the results of quantum-mechanical analysis of molecular electronic structure. This takes place because the results of theoretical analysis of vibrational spectra were drawn basically during the "pre-computer" period.

This report presents the results of vibrational spectra analysis of a vast number of compounds, that have an "ethylene bridge". They range from single-type substitutes to the complex ones. The final compound in this series is lewisite molecule.

The electronic structure analysis of compounds under consideration was performed with the help of "GAUSSIAN" software package. The results are used as zero-approximation for solving direct and inverse vibrational problems, calculation of vibrational-rotational interaction parameters and electro-optical parameters.

The data obtained allow to eliminate several of the above mentioned drawbacks, to perform theoretical analysis of intra-molecular dynamics (force and electro-optical parameters, constants of vibrational-rotational interaction) of the compounds under consideration and their isotopic substituted analogues.

The possibilities for various bases of semi-empirical and ab initio quantum-chemical methods for analysis of electronic structure and spectra for the compounds investigated are found out.

ABSTRACTS
POSTERS - SESSION (2)

Spectroscopy and Chemical Dynamics (2)

-Chemical Reactivity
-Transient Species
-Photophysical & Photochemical processes

2D FT-NIR CORRELATION SPECTROSCOPIC STUDY OF THERMAL AND NEAR-IR PHOTOCHEMICAL GENERATION OF RADICAL IONS IN OPTICALLY NONLINEAR m-NITROANILINE CRYSTALS

P9.1

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Polarized FT-NIR spectra in the 4100-10500 cm^{-1} region of m-nitroaniline single crystals were recorded from 300 to 380 K. The samples were only heated or irradiated at 9700 cm^{-1}, corresponding to the -NH_2 stretching second overtone ($3\nu^{s}_{NH_2}$), and then heated. Direct heating from 325 K until the phase transition (365 K [1]) caused an elevation of the relative background absorbance (ΔA) near 10 500 cm^{-1}.

Further increase in temperature led to decrease of ΔA. Band maxima wavenumbers decreased or increased slightly with temperature. The NIR irradiation of the crystal in conventional spectrophotometer and a subsequent heating resulted in the smaller and different increase of ΔA than in the case of non-irradiated sample. The background elevation is supposed to origin from low-lying electronic transitions (conductivity band) of radical ions generated by irradiation and heating. Aur results indicate that radical ions produced photochemically and thermally are different.

2 D correlation analysis below the phase transition reveals a possibility of new bands appearence. All changes in the spectra with temperature, recognized by 2D correlation analysis, are discussed in view of the plasticity of the m-NA crystal [1], of different ways of radical ions generation stated in [2] and in terms of eventual aggregates formation as in liquid [3,4] and/or ionization like in solid [5]

N-metylacetamid. The role of hydrogen bonding breaking due to -NH_2 proton jumps [1] is also taken into account in the ionization and conductivity of the material.

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P9.2

SPECTROSCOPIC CHARACTERISTICS AND LASER ACTION PROPERTIES OF COUMARIN 540 A IN SOL-GEL

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Out of thousands of organic dyes synthesized over the last hundred years only a few show laser action when excited by Q- switched laser or a pulsed nitrogen laser and still fewer under flash lamp excitation. Organic dyes that show laser action are selected by trial and error. For an efficient working of a laser material it is important to select dyes which have high quantum yield and low lasing threshold. Coumarin dyes or alpha-benzopyrones are known for their strong lasing effect (1-2). It is a class of laser dyes emitting in the blue green region of the spectrum and derived from coumarin - the parent molecule on substitution with auxochromic groups at various carbon positions. Depending on the location and direction of the singlet-singlet (S-S) relative to triplet- triplet (T-T) oscillators within the molecular frame, substitution by the amino auxochromic group may cause T-T absorption bands to move in or out of fluorescence region, or they may be left unchanged (3-4).

An attempt is made to study the spectroscopic characteristics of Coumarin 540 A molecule. Electronic absorption spectra of Coumarin 540 A are measured in the wavelength region 190 – 700 nm in liquid solvents and sol-gel matrix (5). Fluorescence spectrum is measured on exciting Coumarin 540 A doped in solgel by varying the excitation wavelengths. Electronic transitions observed experimentally, are interpreted using the optimized geometries and CNDO/S-CI method (6). Assignments of observed electronic transitions are made on the basis of singlet- triplet electronic transitions. Further, effect of amino substituent on the spectral properties of the parent aromatic molecule are investigated on the basis of molecular structure and spectral predictions for coumarin 540 A as a potential dye laser material are made. These predictions supported by theoretical results are presented graphically with possible arrangements of low energy S-S oscillators relative to T-T oscillators located in the fluorescence region. Depending on short or long axis substitution, the red shifts of the S-S and T-T absorption bands are observed and the importance of these red shifts, as related to the laser action properties are discussed. We have found a good agreement between the experimental and calculated results. Further, coumarin 540 A doped in sol-gel is found to be a strong potential dye laser material.

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INFLUENCE OF THE ENVIRONMENT ON ELECTRONIC STRUCTURE OF ASYMMETRIC AZOBENZENE DERIVATIVES – EXPERIMENT AND QUANTUM-CHEMICAL CALCULATIONS.

P9.3

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Photophysical and photochemical properties of azobenzene derivatives, extensively examined due to emerging possibilities of using the materials in non-linear optics and in data storage [1,2], depend on both, structure of the photoactive molecules and on their interactions with their environment. The purpose of the research reported in this contribution was to investigate the effect of solvents and of substituents in asymmetrically substituted azobenzenes on their geometry and electronic spectra.

The experiment was performed on 4-nitro-4'-aminoazobenzene and a series of 4-X-4'-methoxyazobenzenes (X = F, Cl, Br, NO_2), dissolved is solvents of various polarities (heptane, chloroform and acetonitrile). The spectrum is typical of a *trans* form of azobenzene, with a pronounced π-π^* absorption band peaking at 330-370 nm depending on substituents and solvent, and a weaker n-π^* band around 440-460 nm. After irradiation with UV light (λ = 360nm), a decrease of the intensity of the UV band can be observed, accompanied by a build-up and a slight shift of the VIS band, due to an increase of the concentration the *cis* isomer. The process was found reversible in all samples studied, the reverse reaction being photochemically or thermally driven.

Dipole moments of the ground and lowest excited states, transition energies and electronic transition moments of the compounds under study were calculated using semi-empirical all-valence method (GRINDOL) including the configuration interaction [3]. The ground state geometry of investigated molecules was optimised using the AM1 [4] and *ab initio* [5] methods. The calculations were carried out both for isolated molecules and for molecules in a polar solvent. The QM/LD/MC method [6] (with the discrete representation of solvent molecules) was used to calculate the solvent effect. The result are with reasonable agreement with the experiment.

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P9.4

HIGH PRESSURE LASER PHOTOLYSIS AND ITS APPLICATION IN BIOINORGANIC SPECTROSCOPY

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The impressive development of fast reaction techniques has stimulated a tremendous progress in bioinorganic mechanistic studies. Many such studies concern either ligand susbtitution or electron transfer reactions of coordination compounds due to their fundamental role in biological processes.

Laser flash photolysis is one of the most useful spectroscopic techniques that have been adopted to study fast or very fast thermal processes of biological relevance. Combination of this technique with high pressure instrumentation gives a unique possibility to study the pressure effects on thermal reactions of unstable species generated in solution photochemically. The application of pressure as a physical variable can lead to better insight on volume changes associated with the process studied and can allow the construction of a volume profile. Such data can be employed very successfully to gain detailed information on the reaction mechanism as they exhibit some important advantages over entropy of activation: they can be determined more accurately; their interpretation is less difficult; their value can be correlated with partial molar volumes of reactants and products in the ground state. Therefore, high pressure laser flash photolysis studies may add a decisive dimension to mechanistic studies of some fast or very fast bioinorganic reactions in solution.

In the frame of the poster we present an application of high pressure laser flash photolysis technique in studying the mechanism of NO binding to chosen Fe and Co complexes of biological importance. Studies of the interaction of NO ligand with transition metal complexes, especially metalloporphyrins, are important in understanding the biological role of nitric oxide.

P9.5

SPECTROSCOPIC CHARACTERIZATION OF γ AND α-PIRONES AND THEIR SUBSTITUTED 4-HYDROXY AND 4-METHOXY DERIVATIVES. AN INTEGRATED INFRARED, PHOTOPHYSICAL AND THEORETICAL STUDY

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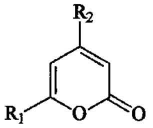
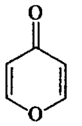
The simple α and γ pirones and the substituted 6-methyl, 4-hydroxy and 4-methoxy α-pirones were investigated in relation to their spectroscopic properties. The characterization involves vibrational and electronic spectroscopy. Raman and IR spectra for the ground electronic state of the studied compounds were obtained (both for the condensed phase and for the molecules isolated in an argon matrix) and assigned, taking into consideration the simulated *ab initio* (6-31G* basis set) data. The most important canonical structure accounting for the properties of the ground state was determined in each case and several photophysical properties were evaluated: the electronic spectra, oscillator strengths and the emission properties (both fluorescence and phosphorescence) in media of different polarity.





γ-pirone

R$_1$= R$_2$= H, α-pirone
R$_1$= CH$_3$, R$_2$= OH, 6-methyl-4-hydroxy- α-pirone
R$_1$= CH$_3$, R$_2$= OCH$_3$, 6-methyl-4-metoxy-α-pirone

Semi-empirical M.O. calculations were performed, and the energy of the electronic transitions compared with experiment. Excellent agreement was observed between the theoretical and experimental results. The origin of the first singlet and triplet excited states is also discussed. It was found that the lowest lying singlet excited state has n,π* character, independent of the solvent used. In contrast, triplet states of π,π* origin were found for the cationic species of 6-methyl-4-hydroxy-α-pirone and its methoxylated derivative, while the neutral forms of the same compounds exhibit phosphorescence lifetimes in the ms range.

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P9.6

SPECTROSCOPY AND PHOTOPHYSICS OF HYDROXYCOUMARINS

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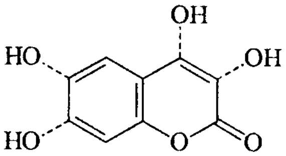
Coumarins, in particular the hydroxycoumarins, are well known compounds occurring in nature, for example in plants of the *Umbelliferae* family. The interest in these compounds is however much more diversified, covering fields as diverse as sun screen formulations and laser dyes.

In this work we report the ground-state (S_0), excited singlet and triplet state (S_1 and T_1) properties of several hydroxycoumarins (HC) in different media. Both S_0 and excited state pKa were determined and it is seen that in general for the HC compounds here studied the S_1 state is more acidic than S_0. In S_0 only two absorbing species were observed, which are atributed to neutral and anionic forms. In the S_1 state, depending on the HC considered, an additional tautomer can be present. The nature of this third species is discussed.



Fluorescence data, including fluorescence quantum yields and fluorescence lifetimes were studied to further elucidate the mechanisms involved. The triplet state was also considered using triplet-triplet absorption and phosphorescence data. For the above results, the nature and number of species existing in the protonation equilibria in the triplet state was also addressed.

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ROOM TEMPERATURE AND LOW TEMPERATURE ABSORPTION AND EMISSION SPECTRA OF SOME POLYPYRIDYLRUTHENIUM(II) 3.2.1 COMPLEXES

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Although the spectra and photophysics of polypyridylruthenium(II) complexes have been studied for over 40 years,[1] they still attract wide interest. This is stimulated both by the wide range of applications, varying from solar energy conversion[2] to oxygen sensors[3] and potential elements of polymeric light emitting devices.[4] For practical applications there is a need for developing new complexes which are stable to photosubstitution, but which can readily be joined to polymeric or supramolecular systems. We have synthesised a series of complexes of type $[Ru(tpy)(L\text{-}L)(py)]^{2+}$, where tpy and py are 2,2',2"-terpyridine and pyridine, and L-L represents the bidentate ligands bipyridyl, 4,4'-dimethylbipyridyl, 4-nitrobipyridyl, oxalate and acetylacetonate.[5] For convenience we refer to these as 3.2.1 complexes, where the number refers to the denticity of the ligands. We report the electronic absorption and emission spectra of these compounds. In all cases, the lowest energy absorption band corresponds an intense $Ru(d\pi) \rightarrow (tpy)\pi^*$ MLCT transition. This shows a slight red shift and becomes sharper on decreasing temperature. Marked differences were observed between the spectra of the oxalate and acetylacetonate complexes and those of the bipyridyl derivatives. Further differences were observed in the effect of solvent polarity on these bands, and we suggest that these are related to the electron donating character of these nonchromophoric ligands. Luminescence in polypyridylruthenium(II) complexes results from phosphorescence from the lowest MLCT triplet state. The 3.2.1 complexes show weak phosphorescence at room temperature, but this increases dramatically on decreasing the temperature to 77K. Again, marked differences are observed in the spectra of the acetylacetonate and oxalate derivatives compared with the other complexes. The possibility of using this to modulate emission colour in light emitting devices will be discussed.

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P9.8

POLARIZED ABSORPTION AND FLUORESCENCE OF STILBENE HOMOLOGUES ORIENTED IN PERHYDROTRIPHENYLENE SINGLE CRYSTALS

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Crystalline perhydrotriphenylene (PHTP) enables specific host-guest architectures, where linear or rod-shaped guest molecules are included in channels in between the columns formed by the PHTP-host. These systems are of interest for investigations of intermolecular guest-guest interactions and for applications in nonlinear optical devices, microlasers, and electroluminescent nanotube crystals Thus, high dichroic ratios and/or high fluorescence quantum yields of these materials are desirable.

In this contribution we describe optical properties of the first members of oligo(p-phenylenevinylene)s, i.e. stilbene, p-distyrylbenzene, and p-distyrylstilbene included in PHTP single crystals. The polarized absorption and fluorescence spectra of individual crystal needles are highly dichroic ($D \approx 20$) indicating orientations of the guest transition dipoles parallel to the PHTP-column axis. Any torsional motions of the guests resulting in fluorescence quenching or *trans-cis* photoisomerization are highly suppressed, also in the case of stilbene.

The vibronic fine structures of the low temperature spectra at $T = 10$ K reveal some guest-guest intermolecular electronic coupling, but compared to the pure condensed phases of oligophenylenevinylenes the electronic interactions are extremely weak. However, long range interactions resulting in excitation energy transfer can be analyzed very well. For this kind of investigations the system PHTP/stilbene was doped with small molar fractions ($x = 10^{-4} - 5 \cdot 10^{-3}$) of distyrylbenzene that acts as efficient energy acceptor. From time-resolved polarized fluorescence measurements the complete transfer and deactivation kinetics of the doped system could be analyzed.

DYNAMICS OF ELECTRONIC ENERGY TRANSFER IN LINEAR CHAIN POLYMERS

P9.9

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Electronic excitation transport between chromophores attached to polymer chains has been widely used as a structural probe. The time dependence of the donor and trap fluorescence intensities following pulse excitation can be related to the interchromophore separation through the Forster transfer rate. Such experiments are generally performed under very dilute conditions, allowing intermolecular excitation transport to be neglected.

In the models to be reported, the following types of chromophore attachment to polymer molecules are considered: First, every polymer molecule contains exactly one donor and one trap chromophores attached to the ends of a chain. Some biomolecules fall in this category, as well as fluorescent tagged polymers that are synthesized from macromolecules having functional groups of different reactivity towards donor and traps. Second, donor and trap chromophores are randomly distributed among the sites of the polymer molecule. The occupancy of a particular site is independent of the type or number of chromophores substituted at the other sites. Third, all sites of polymer molecules are occupied by donor and acceptor chromophores, the distribution of chromophores is random, and the trap concentration is small. Such polymer molecules can be considered as a one-dimensional linear lattice. Aromatic polymers are an example of such systems.

All these three models of chromophore attachment were investigated. Isotropic dipole-dipole interaction between chromophores was assumed. Ideal (Gaussian) and nonideal (with volume interaction) polymer chains were investigated.

In the static regime, when the polymer chain movement is frozen during the excited-state lifetime of chromophores, simple analytical equations for luminescence kinetics valid for all times with precision higher than 1% are obtained. Using these kinetics one can obtain the radius of gyration and determine what kind of chain (ideal or nonideal) is under investigation. We obtained also analytical results for the kinetics of luminescence anisotropy. The influence of inhomogeneous broadening of chromophore spectra on luminescence kinetics was also investigated.

In the dynamic regime (when flexible polymer chain changes its configuration during the excited state lifetime of donor chromophore) the diffusional (Brownian motion of links containing chromophores) and hopping (transitions between the stable polymer conformations are sudden and random both in time and in space) limits of chain movement were investigated. Equations were written and solved analytically and numerically. The values of the diffusion constant and of the time of conformation changing, at which these kinds of polymer movement must be taken into account, were obtained.

We showed that luminescence kinetics becomes exponential (for the first and third models of chromophore attachment) if the chain movement is fast enough. The analytical equations for this kinetics (ideal and nonideal polymer chains) were obtained.

P9.10

SOLVATOCHROMISM OF THE ELECTRONIC SPECTRA OF TWO DYES (A SQUARAINE AND A CYANINE)

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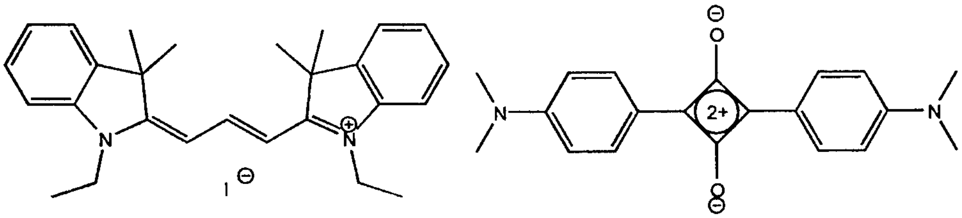
The squaraines and cyanines constitute two families of organic dyes with a centro-symmetrical structure. The two dyes studied, shown in Fig. 1, are representative examples of these two families. The electronic spectra of these two dyes appear in the red and the transitions are intense. However the nature of the two transitions is different: while in the 1,1'-diethyl-3,3,3',3'-tetramethylindocarbocyanine ***diIC₂(3)***, a $\pi^* \leftarrow \pi$ transition is observed; in the bis[4-(dimethylamino)phenyl] squaraine ***HSq***, the transition is of the charge transfer type. In this communication, we present results on solvent effects in the electronic spectra of these two dyes.



diIC$_2$(3) **HSq**

Fig. 1 – Structure of the 1,1'-diethyl-3,3,3',3'-tetramethylindocarbocyanine ***diIC$_2$(3)*** and bis[4-(dimethylamino)phenyl] squaraine ***HSq***.

The different nature of the transitions leads to different behaviours. While in the ***diIC$_2$(3)*** the solute/solvent interactions are mainly dispersion forces, in the ***HSq*** hydrogen bond interactions are observed [1]. Also the solvent polarity character influences the ***HSq*** spectra, in a way unexpected for a centro-symmetrical molecule. The results are explained on the basis of strong quadrupole changes in the ***HSq*** case, which are not observed in the ***diIC$_2$(3)*** case. The thermochromism of the ***diIC$_2$(3)*** will also be presented and analysed in the framework of the coordinate configuration model [2], showing also the importance of the internal nuclear fluctuations on the electronic transition of such dyes.

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MOLECULAR TWIN-DONOR ENERGY TRANSFER

P9.11

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In the study of molecular photoprocesses, attention has recently been focused on a nonlinear analogue of resonance energy transfer. At sufficiently high levels of laser excitation, it has emerged that the absorption of radiation by two chromophore units within a molecular array can lead to a process in which both act as donors, simultaneously furnishing excitation energy to a third, acceptor group[1]. The result of this energy pooling is the acquisition by the acceptor of an energy exceeding that of the input photons, which can lead to blue-shifted fluorescence (or further photochemistry). In this sense the fundamental mechanism is a molecular counterpart to that responsible for laser upconversion processes in doped rare earth crystals.

Several conditions must be met for molecular twin-donor resonance energy transfer to be effective, namely: (i) close proximity between the two donor molecules and an acceptor molecule; (ii) overlap between the two-photon absorption spectrum of the acceptor molecule and the sum of the donors emissions; (iii) co-existence of the two donors in the excited state for some time; (iv) negligible back-transfer. An experimental situation where molecular twin-donor resonance energy transfer could be effective was investigated by time-resolved fluorescence. It consists of fullerenes as donors, and aromatic compounds as acceptors, solubilized in micelles at low temperature.

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P9.12

IFLUENCE OF EXCITING CONDITIONS ON PHOTOSTABILITY OF DIMETHILAMINOSUBSTITUTED PYRIDYLPHENYLOXAZOLE.

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Many problems are solved presently in different branches of science and engineering using the dye lasers. However, photostability of this active media is low. Increasing of photostability requires reseach of photochemical and photophysical processes depending on conditions of excitation and radiation. Study of reason to form TICT conformation is scientific interest. Moreover, the number of molecules providing TICT conformation lasing is limited. The structure there conformation is not determined and is discussed in scientific literature.

The experimental determination of emission characteristics and photostability was maked for hexan, ethanol, acetonitril solutions of dimethilaminosubstituted pyridylphenyloxazole – 4PyPON$(CH_3)_2$ used excimer XeCl laser at λ=308 nm with $\tau_{1/2}$=15 ns, E_{out}=40 mJ/pulse. Two geometry of the pumping beam was used and density of pump W are to 180 MW/cm^2. Quantum-chemical calculations involved below are performed using the semiempirical quantum chemical INDO method with the spectroscopy parametrization according. Specific interaction was calculated by method molecular electrostatic potential (MEP).

It is shown that nature 4PyPON$(CH_3)_2$ state in polar and nonpolar solution is different. This molecule has the bond emission in the region 565 nm in ethanol and 420 nm in hexan. Theoretical and experimental spectroscopic investigations 4PyPON$(CH_3)_2$ has demonstrated that TICT is formed conformation in polar medium.

The efficiency coefficient of lasing has the maximum in the region $20\div30$ MW/cm^2 versus the pumping intensity in polar medium. The maximum efficiency coefficient of lasing is observed in acetonitril where the molecule to exist in TICT conformation. Photostability and characteristics of lasing was determined for various values of the pumping power density ($15\div180$ MW/cm^2). Investigation of 4PyPON$(CH_3)_2$ under high power excitation showed that quantum of phototransformation is correlated drive emission. Quantum yield phototransformation and relative quantum yield photoproducts and a resource of active media ware determined. Photostability of active media is evaluated in depending on geometry pumping beam and excited volume.

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INTRAMOLECULAR TRIPLEX FORMATION OF THE G*G•C TYPE: A SPECTROSCOPIC STUDY

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Short homopurine-homopyrimidine regions in DNA have attracted a great deal of attention in connection with their possible role in gene regulation in eukaryotes (1). Recognition of nucleic acids by triplex-forming oligonucleotides occurs by hydrogen bonding between oligonucleotide bases and purine bases in the major groove of the target duplex. Triple helix formation arises in either of two patterns, termed the pyrimidine motif and the purine motif (2). To promote triplex formation with cytosine-containing oligonucleotides, a slightly acidic environment is required. In contrast, the purine motif is pH-independent and has been used far more often for successful *in vivo* inhibition of transcription.

Although triplexes based on the purine motif have been studied by vibrational spectroscopy, the origins of some characteristic spectral features are still unclear. This is the case of triple helices having the G*G•C triplet, where two different hydrogen bonding schemes have been suggested between the two guanine bases (Fig. 1).

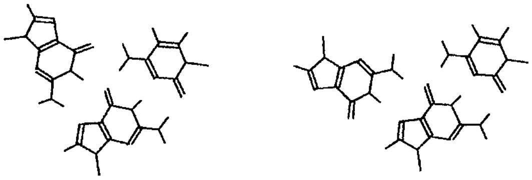

Fig. 1. Hoogsteen (*left*) and reverse Hoogsteen (*right*) forms of G*G•C triplet

The present work was therefore undertaken to calculate in-plane normal mode frequencies for these triplet forms by using a valence force field that incorporates transition dipole coupling for guanine C=O groups in the Hoogsteen structure. This coupling mechanism is shown to give a reasonable explanation of the νC=O splitting for the Hoogsteen form, unlike the reverse Hoogsteen one where carbonyl coupling is absent.

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P9.14

SPECTROSCOPIC INVESTIGATION OF THE RING-PUCKERING AND RING-FLAPPING VIBRATIONS OF PHTHALAN, 1,3-BENZODIOXOLE, COUMARAN, AND INDAN IN THEIR S_0 AND S_1 (π, π^*) ELECTRONIC STATES

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The far-infrared and Raman spectra of phthalan, 1,3-benzodioxole, coumaran, and indan vapors have been recorded and analyzed to determine the two-dimensional potential energy surfaces for the ring-puckering and ring-flapping vibrations in their S_0 electronic ground states. Phthalan is planar while indan and coumaran are puckered due to methylene-methylene torsional interactions. 1,3-Benzodioxole is also puckered due to anomeric effects which are somewhat suppressed by the presence of the benzene ring. Electronic absorption spectra and laser induced fluorescence spectra of jet-cooled molecules were recorded to determine the puckering and flapping levels in the $S_1(\pi, \pi^*)$ excited states of these molecules. In the excited states the flapping frequencies drop to lower frequencies reflecting the decreased rigidity between the two rings. For phthalan the ring-puckering motion also has a stiffer potential energy function. For 1,3-benzodioxole in the $S_1(\pi, \pi^*)$ state the anomeric effect is less suppressed by the benzene ring and the barrier to planarity is increased. *Ab initio* calculations were carried out for both ground and excited states for these molecules. For the ground state the agreement between observed and predicted barrier heights is excellent.

ANOMALOUS SIMPLICITY OF THE Ã-X DISPERSED FLUORESCENCE SPECTRUM OF $^{13}C_2H_2$

P9.15

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In the past several years, we have gained a detailed and essentially complete picture of the short-time vibrational dynamics of acetylene below 15,000 cm^{-1} of internal energy.[1-4] We are now moving towards higher energy, with the particular goal of investigating how the energetic feasibility of acetylene-vinylidene isomerization is manifested in our frequency domain spectra. A major portion of our effort is being directed towards $^{13}C_2H_2$, as opposed to $^{12}C_2H_2$, which had previously been our exclusive focus. The choice of $^{13}C_2H_2$ is motivated largely by the possibility of observing nuclear permutation tunneling splittings in high resolution spectra as well as the unexpected simplicity in spectra reported.[5]

The first step in studying $^{13}C_2H_2$ has been to record a high quality dispersed fluorescence (DF) data set, similar to the one, which provided our recent insights into $^{12}C_2H_2$ dynamics. DF spectra were recorded from 6 different vibrational intermediate levels and we have used pattern recognition algorithms (Extended Cross Correlation) to gain a broad overview of the short-time vibrational dynamics.[5] Moreover, we have developed an effective Hamiltonian model which describes our DF data to with 1.3 cm^{-1}. Upon close inspection, the dynamics that we observe in $^{13}C_2H_2$ are noticeably *simpler* than the dynamics in $^{12}C_2H_2$. This unexpected discovery is explained in terms of a nearly complete absence of energy flow from the bend modes of $^{13}C_2H_2$ to the stretch modes. The stretch-bend interactions are "turned off" because one key anharmonic resonance, the "3,245" resonance, which is responsible for these interactions in $^{12}C_2H_2$, is detuned in $^{13}C_2H_2$. In $^{12}C_2H_2$, $\omega_3-(\omega_2+\omega_4+\omega_5)\approx 2$ cm^{-1}, which makes the resonance strong and pervasive; in $^{13}C_2H_2$, the energy gap is ≈ 60 cm^{-1}, and the resonance has little impact on the short-time dynamics.

The relative simplicity of the dynamics in $^{13}C_2H_2$ is particularly noticeable above 15,000 cm^{-1}, which is beneficial for attempting to observe the sudden changes in the unimolecular dynamics that we expect will be related to isomerization. Thus far, we have not detected any sudden changes in dynamics up to ~18,000 cm^{-1}. Nonetheless, it is intriguing that the major features of the DF spectra remain unchanged up to ~18,000 cm^{-1}, indicating no major role for vinylidene in the short-time dynamics (~1 ps) as sampled by the relatively low resolution DF spectra.

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P9.16

STUDY OF THE PHOTOPHYSICAL PROPERTIES OF 3[2-(DIETHYLAMINO)ETHYL]-7-HYDROXY-4-METHYLCOUMARIN HYDROCHLORIDE

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Steady-state and time resolved emission spectroscopic techniques at 77K and molecular orbital calculations using AM1-MOPAC/93(1), HAM/3-CI(2) and ZINDO/S-CI(3) have been used to study the 3[2-(Diethylamino)ethyl]-7-hydroxy-4-methylcoumarin hydrochloride (C^+), the monocation form, in different environments. of aqueous medium. The monomer species of (C^+) was determined, in ethanol, while the monomeric form of the complex formed between free base form (C) and ethanol through hydrogen bonded (C-H) was determined, in H_2SO_4 0.5N, the dication (CPZ^{++}) was found and in buffer solution pH=11.8, the free base was dominant. The photophysical properties of all species were determined and we verified that each one of them displays distinct photophysical properties from one to the other. For example, for (C^+), the lowest electronic singlet state S_1 is (n,π^*), with energy 3.153 eV and the lowest electronic triplet state $T_1(\pi,\pi^*)$ with energy 1.814 eV and it is the first order spin-orbital coupling between S_1 and T_1. In this case, the excitation energies calculated by HAM-CI for all species of this coumarin is in accordance with the experiment and is even better than those calculated by ZINDO/S-CI. On the other hand, the most photoactive molecular region by HAM/3-CI calculations, involve the C_3=C_4 of the pyrone ring, the O of the carbonyl, and N of the tertiary amine.

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SPECTROSCOPIC STUDIES OF 9,10-PHENANTHRENEQUINONES IN SOLUTION AND ON THE SURFACE OF SILICA

P9.17

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Quinones are well known class of ketones useful in photoreduction reactions such as electron transfer[1] and hydrogen abstraction[2]. Spectroscopic properties of symmetric 9,10-Phenanthrenequinones with methoxy, chloro and methyl substituents (figure 1, inset) are reported. The substituent effects on the reactivity towards the hydrogen atom abstraction processes are discussed taking into account the photophysical data. The triplet state was studied in benzene, chlorobenzene and acetonitrile solutions as well as on the surface silica using nanosecond laser flash photolysis in transmitance, emission and diffuse reflectance modes. The time resolved spectra (TRS) are identical in solution and on porous Si-6 showing absorption band maxima in the range of 460-480 nm and 640-660 nm (figure 1). By contrast, triplet lifetimes vary with the environment and temperature from few microseconds in solution to hundred microseconds on silica.

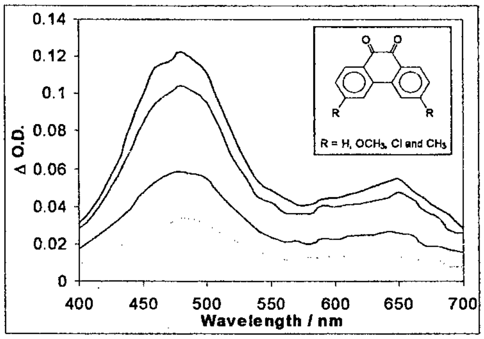

Figure 1 – TRS of the 3,6-Dimetoxy-9,10-Phenanthrenequinone triplet state on surface of silica at different times (microseconds)

The photophysical behavior of Phenanthrenequinones studied in the presence and absence of oxygen will be interpreted on the basis of the electronic nature ($n\pi^*$ and/or $\pi\pi^*$) of their excited state.

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P9.18

DYNAMICS AND MECHANISM OF THE HETEROGENEOUS ELECTRON TRANSFER OF CYTOCHROME C ON ELECTRODES COATED WITH SELF-ASSEMBLED MONOLAYERS. A TIME-RESOLVED SURFACE ENHANCED RESONANCE RAMAN STUDY

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The heterogeneous electron transfer (ET) of cytochrome *c* (Cyt-*c*) adsorbed on an rotating Ag electrode coated by self assembled monolayers (SAMs) of ω-carboxyl alkanethiols of different chain lengths was studied by surface-enhanced resonance Raman (SERR) spectroscopy using 413 nm excitation. When Cyt-*c* is adsorbed on the bare Ag electrode or on coated Ag electrodes with short chain SAMs, a conformational equilibrium of the protein is observed by SERR spectroscopy. These conformational changes do not involve denaturation and are actually of the same kind as those found upon binding of Cyt-*c* to its natural redox partner cytochrome *c* oxidase. However, no conformational changes are induced upon binding to SAMs of longer chain lengths (≥ C_{11}), indicating that these processes depend on the strength of the electric field. SERR spectra measured as a function of the potential yield almost ideal Nernstian behavior (n = 0.96) ruling out any heterogeneity in the redox potential of the adsorbed species. The measured redox potentials show a chain length dependent negative shift due to the potential drop produced by the spacer. A simple model accounting quantitatively for this phenomenon will be presented.

The dynamics of the ET process of the adsorbed Cyt-*c* was studied by time-resolved SERR spectroscopy. In this technique the SERR spectra are probed at various delay times subsequent to a rapid potential jump. For SAMs of 11-mercaptoundecanoic acid, small potential jumps to the redox potential (i. e., 40 mV) yield a relaxation process that could exclusively be ascribed to the heterogeneous ET with a formal heterogeneous rate constant of 43 s^{-1}. Applying larger potential jumps (i. e., 170 mV), without changing the driving force of the ET reaction, the analysis of the time-resolved SERR revealed an additional slower process that is attributed to a potential-dependent re-distribution between (two) different species of the adsorbed Cyt-*c*. These species exhibit identical heme pocket structures but display different ET kinetics, most likely, due to different orientations of the heme relative to the coated electrode.

These results show that time-resolved SERR spectroscopy is a powerful tool to analyze complex interfacial processes on mechanistic basis, since it provides simultaneously kinetic, thermodynamic and structural information of the different adsorbed species.

COMPARISON OF FT RAMAN SPECTRA OF SOME 5-NITROQUINOXALINES AND THEIR ELECTROPOLYMERS

P9.19

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The set of five 5-nitroquinoxaline derivatives (Fig. 1) 2-,3- disubstituted with 2-pyrryl (A), 2-furyl (B), 2-thiophenyl (C), 2-phenyl (D) and 2-pyridyl (E) groups has been newly synthesized to test their capabilities of recognizing and sensing negatively charged species [1].

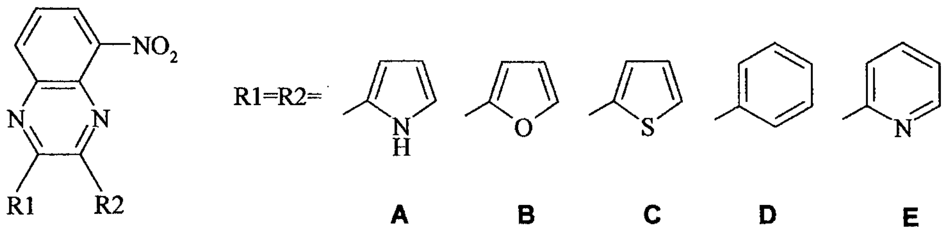

Fig. 1 - 5-nitroquinoxaline derivatives

FT Raman spectroscopy was used to characterize these new species and to investigate their structure. The Raman spectra of five 2,3-disubstituted 5-nitroquinoxalines has been mutually compared and the assignment of individual bands has been done on the basis of vibration modes attributed to characteristic bands of other quinoxaline derivatives by Cheeseman et al. [2].

The 5-nitroquinoxalines were electrochemically reduced to 5-aminoquinoxalines and electropolymerized on the gilded Pt electrode (ca. 2-μm thick porous gold layer) to form polymerized films. The gilded substrate enables to obtain FT SERS spectra of polymers. Comparing the FT SERS spectra of polymers with FT Raman spectra of monomers we have suggested the mechanism of electropolymerization. While the pyrryl derivative (Fig. 1 A) is polymerized via pyrroles, the other derivatives are polymerized via the amino groups to form substituted polyanilines. The ion selectivity of prepared films will be further studied by potentiometry.

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P9.20

$(H_2O)_2$ CO TRIMER – CYCLIC OR LINEAR ?

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In this poster we report *ab initio* predictions of the minimum energy structure of the $(H_2O)_2$ CO cluster, its stationary points and low-energy tunneling pathways. Structures corresponding to the stationary points were optimized with the second-order Møller-Plesset theory, while the corresponding interaction energies and binding energies were computed using the coupled cluster method restricted to single, double and noniterative triple excitations using aug-cc-pVDZ basis set. The global minimum on the potential energy surface of the trimer corresponds to a cyclic triangular hydrogen-bonded structure with C atom of CO bounded to the proton-acceptor water molecule. It was found that the PES of this cluster shows three low-energy pathways connecting to the enantiomeric minimum energy structures (A).

The heiths of the barriers corresponding to these transition states are quite low, so it should be possible to observe spectroscopic transitions resulting from the tunneling between the equivalent equilibrium structures via these pathways.

Additionaly we investigated the transition between (A) and (B) structures (see Fig.1) and localized the transition state for this path.

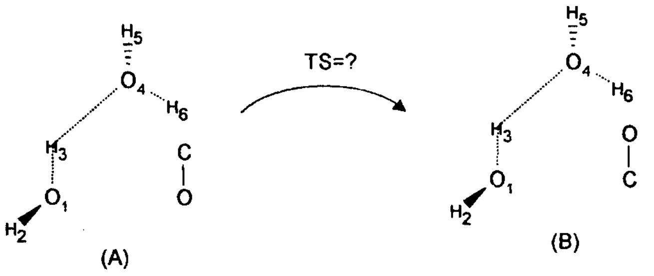

Fig. 1 Global (A) and local (B) minimum structures of $(H_2O)_2$ CO trimer

THEORETICAL STUDIES ON TAUTOMERISM AND IR SPECTRA OF C-5 SUBSTITUED IMIDAZOLES

P9.21

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Imidazole ring is frequent moiety of numerous drugs (for example cimetidine, tizamidine, oxymethazoline) and bioactive molecules (like histamine). Due to two nitrogen atoms present in its five membered unsaturated imidazole ring, if unsymmetrically substitued, imidazole exhibits tautomerism at nitrogen atoms. It means that either to N1 or to N3 the hydrogen atom may be bound to.

So far, there is a lack of the theoretical investigations of influence of a substituent at the position C-5 on imidazole tautomerism. In the present studies, we investigate influence of the -NH_2, -OH, -COH, COF, -COOH, -$COONH_2$, -CN, -F, -Cl, -CH_3, and -NO_2 substituent. These substituents have different character and affect differently the imidazole electronic structure (Table 1). The relations of the tautomer type and its infrared spectrum with character of the substituent and theoretical method used is discussed.

Table 1. Energy difference between the N1 and N3 imidazole tautomers

Substituent at C-5	ΔE (Kcal/mol)	
	RHF/6-311++G**	MP2/6-311++G**
BH_2	-4,38	-4,59
COOH	-2,053	-0,932
COH	-1,443	-1,506
COF	-1,443	-1,261
NO_2	0,315	0,99
CH_3	0,419	0,514
CN	1,075	1,074
NH_2	1,419	1,057
$CONH_2$	1,92	1,738
Cl	2,93	2,039
F	4,428	4,813
OH	8,816	5,072

P9.22

DIOXYGEN BINDING AND STRUCTURAL PECULIARITIES OF *meso*-PYRIDYL SUBSTITUTED Co(II)- AND Fe(II)-PORPHYRINATES IN THEIR SUBLIMED LAYERS.

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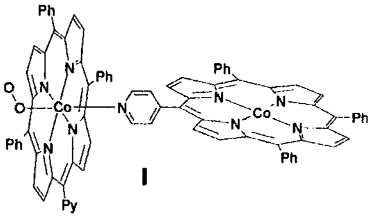
Thin layers of porphyrin-like compounds has gained much interest in the past decade because of their potential application in photovoltaic cells, gas sensing devices, heterogeneous catalytic systems etc. On the other hand, studies of dioxygen binding to metalloporphyrins provide opportunities to attack the fundamental problems of the biological oxygen carriers and oxygenases.

In this report we present the FT-IR and UV-Vis data that indicate the specificity of reversible dioxygen binding by the low-temperature (T=77 K) sublimed layers of *meso*-tetra-pyridylporphyrinatoiron^{II} (FeT4PyP) and *meso*-mono-pyridyl-tri-phenyl-porphyrinato-cobalt^{II} (CoMPyTPP). For these compounds the $\nu(O_2)$ values of coordinated O_2 are lower and thermal stability of dioxygen adducts substantially higher than those for the sublimed layers of corresponding tetra-phenyl-substituted derivatives [1, 2]. These results indicate that dioxygen occupies the 6th coordination site in metal coordination sphere in which the 5th site is occupied by the pyridyl nitrogen of the adjacent molecule.



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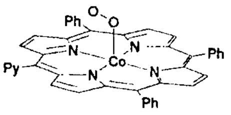

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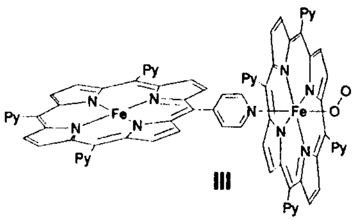

III

This conclusion was confirmed by the experiments with action of O_2 on the sublimed layers containing the five-coordinated PyCoTPP. In the freshly sublimed layers of CoMPyTPP both types of five-(II) and six-(I) coordinated complexes were observed. With the passage of time, the fraction of five-coordinated species decreases, while six-coordinated increases. On the air FeT4PyP's (III) layers are slowly oxidized forming μ-oxo-species and lose O_2-binding ability. At the same time, the layers of CoMPyTPP conserve this property over prolonged period and can serve as a good prototype of the synthetic oxygen carriers.

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SUBLIMED LAYERS OF *meso*-TETRAARYLPORPHYRINATOMETALS AS A TEMPLATES FOR THE SYNTHESIS OF AXIAL COMPLEXES WITH MIXED LIGANDS

P9.23

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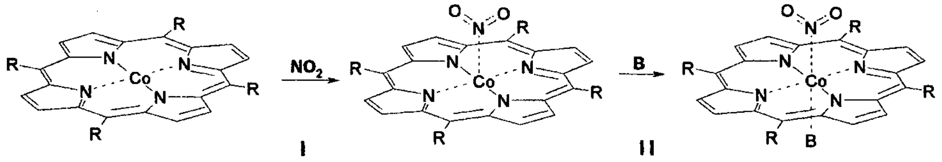
The layers of *meso*-tetraarylporphyrin metallocomplexes obtained by sublimation on to low temperature surface have microporous structure that enables easy diffusion of potential ligands to the layers bulk and spectral characterization of adducts thus formed. It was previously shown [1] that the interaction of *meso*-tetraphenylporphyrinatocobalt^{II} sublimed layers (CoTPP) with NO_2 may be interrupted on the stage of 5-coordinated nitro-complex formation (scheme, stage **I**).



R = C_6H_5, B = NH_3, $C_5H_{11}N$, C_5H_5N

Here we demonstrate the FT-IR spectroscopic evidences that this complex easily transform to 6-coordinated nitro-ammine complexes in the atmosphere of corresponding amines (scheme, stage **II**). This process is accompanied by the expected shifts of bands assigned to fundamental vibrations of the coordinated NO_2 moiety and the frequencies of these bands coincide with the reported literature values for some of these complexes. The assignments were also confirmed by the use of $^{15}NO_2$ isotopomer.

It should be emphasized that CoTPP·NO_2 layers, in contrast to CoTPP, preserve their ability to interact with the additional ligands over prolonged time. Hence, 5-coordinated axial complexes of metal-*meso*-tetraarylporphyrins in accordance with the prediction of [2], conserve the microporousity of their structure and can serve as a templates for designing of the metalloporphyrins axial complexes with the mixed ligands.

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P9.24

PALLADIUM AS A CATALYST IN AN ORGANIC MATRIX

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One of the main goal of studying supported transition metal complex catalysts is to anchore the complex to a support, which can be an organic polymer or an inorganic oxide [1]. As organic matrices, both natural or synthetic polymers were applied, for example cyclodextrine [2], polyamides [3], etc. In our forthcoming paper [4] we report about an organic matrix supported Pd catalyst, in which an adduct was formed from the $PdCl_2$ and the monomer of the support before polymerization. The catalytic activity and selectivity of the Pd catalysts prepared are demonstrated in a couple of hydrogenation reactions in the liquid-phase, under mild condition.

For organic matrix preparation three aromatic amines (aniline, 3-aminophenol and 1,3-phenylenediamine) were chosen as starting materials. In a first step adducts were prepared from the selected amines and $PdCl_2$, then, in a polycondensation reaction those adducts were polymerized with formaldehyde. This latter reaction were carried out with the pure amines to prepare reference polymers.

The structural changes as a result of adduct formation and the polycondensation reaction was followed by IR spectroscopy. The interaction arisen between $PdCl_2$ and the -NH_2 and -OH groups of the amines caused essential variations in the vibration patterns. Spectra of the Pd-containing polimers were compared to the appropiate adducts and the $PdCl_2$ free polimers. Differences will be discussed.

The nitrogen adsorption/desorption properties of those adducts, $PdCl_2$-containing polimers and $PdCl_2$-free polimers were also studied. The specific surface area was calculated from monolayer capacity. From the desorption branch of the isoterms the pore size distribution was derived and mesopore size calculations were also performed.

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IR INVESTIGATION OF THE TRANSFORMATION OF PROPYNE TO PROPADIENE ON SOLIDS

P9.25

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In 1959, Cordes and Günzler published experimental data on the equilibrium concentration of propyne and propadiene observed over various heterogeneous catalysts [1]. In the work leading to this contribution spectroscopic experiments were carried out in order to reinvestigate both the surface intermediates and the influence of acid-base character of the catalyst in the reactions of propadiene and propyne.

The solids used in the experiments were as follows: CaO, MgO, ZnO, and NaY-, CaY-, MgY- and ZnY-FAU type zeolites. For the IR spectroscopic measurements, self-supported wafers were pressed from the solids with thickness of 10 mg/cm^2. After pretreating the wafers in an *in situ* IR cell in vacuum, the reactants, either propyne or propadiene, were introduced into the cell and the spectra were recorded at various reaction times and temperatures. The gas phase spectra were also taken after each treatment.

Metal oxides, such as CaO, MgO and ZnO, and zeolites NaY-, CaY-, MgY- and ZnY-FAU were studied. The specific surface areas of zeolite samples were found in 300-500 m^2/g region, while the oxides possessed much smaller values.

When propadiene was used as the starting adsorbent, their bands decreased in intensity and that of the product propyne increased. The transformation of propadiene was followed by monitoring the band due to C=C bond at 1959 cm^{-1} in the gas phase spectrum. Upon adsorption this band was shifted to 1945 cm^{-1}. The formation of propyne adsorbed was evidenced by giving rise to a band at 2115 cm^{-1} corresponding to the C=C bond, which appeared at 2142 cm^{-1} in the spectrum. These features were found on all the catalysts used.

For the adsorption of propyne similar spectral changes were observed, but in the reversed direction. From these follows that the surface transformations of the reactants take place independently on the nature of the surface.

In some cases bands at 3250, 2920, 2855 and 1865 cm^{-1} were simultaneously observed. This spectral phenomenon might be attributed to the formation of propargyl anion on the surface [2].

Transformation of propyne to propadiene and propadiene to propyne occurs on both acidic and basic contacts, however, their rates are different. Among the surface species generated propargyl anions were also assumed.

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P9.26

AN FT-IR STUDY ON DIELS-ALDER REACTIONS CATALYSED BY HETEROPOLY ACID CONTAINING SOL-GEL SILICA

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Although Lewis acid catalysts have been known [1] to be effective for Diels-Alder type cycloaddition reactions for quite a while, solid acids have only recently been considered for such purposes.

In this contribution we present our FT-IR investigations on the reactions of 1,3-cyclopentadiene and 1,3-cyclohexadiene with acrolein and methyl-vynil-ketone catalysed by phosphotungstenic acid built into a silica support both by conventional impregnation and one-step sol-gel incorporation. One of the reactions performed is depicted in Fig. 1., while Fig. 2. presents representative reaction spectra recorded *in situ* on a Mattson Genesis FT-IR 1 instrument.

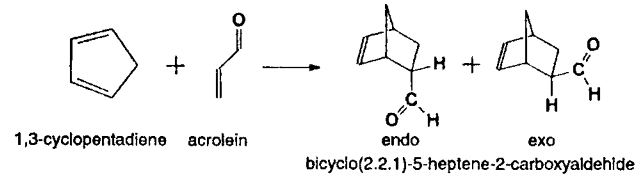
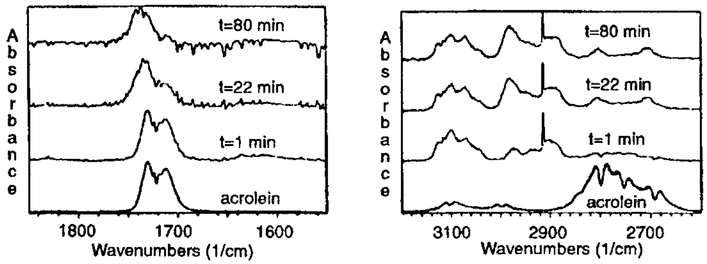


Fig. 1 – One of the reactions studied is that of cyclopentadiene and acrolein



a) b)

Fig. 2 – Gas phase FT-IR spectra (a: C=0 region, b: C-H region) of the propagation of the reaction depicted on Fig. 1 as a function of time

IR spectroscopic results are in good agreement with data obtained from independent experiments (GC and acidity measurements), and indicate that our catalysts are active in all selected reactions. Higher heteropoly acid loading and better stability can be achieved via the sol-gel method than by impregnation, therefore we continue our catalytic Diels-Alder studies in this direction.

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THE PHONON-ASSISTED PROTON TRANSFER BETWEEN HYDRAZINIUM CATIONS IN $(N_2H_5)_2HMF_6{\cdot}2H_2O$ ($M\in$\{Ga, Al, Fe\}) TYPE COMPOUNDS. FT IR AND QUANTUM THEORETICAL STUDY

P9.27

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Room and low temperature (~100 K) Fourier transform infrared spectra of a series of compounds with a general formula $(N_2H_5)_2HMF_6{\cdot}2H_2O$ (where $M\in$\{Ga, Al, Fe\}) were recorded. Special emphasis was put on the region of appearance of bands due to the ν(N-N) modes of hydrazinium cations. Our present investigation of the FT IR spectra of the mentioned compounds further supports the recently outlined conclusions [1] regarding the $N_2H_5^+\cdots H^+\cdots N_2H_5^+$ hydrogen bond potential well based on Raman spectroscopic data. The appearance of two bands corresponding to the ν(N-N) modes in the low temperature FT IR spectra that merge into one upon heating is a clear evidence of a symmetric potential well through which a phonon-assisted proton transfer occurs at higher temperatures. In order to get a deeper insight into the dynamics of the proton transfer process, the FT IR spectra were also recorded at variable temperatures (from ~100 to 300 K, at 10 K intervals). The dependence of the ν(N-N) bands splitting as well as of the intensity ratio on the temperature was followed within this temperature interval.

A semiempirical and *ab initio* HF SCF study of the proton transfer potential within the $N_2H_5^+\cdots H^+\cdots N_2H_5^+$ system was performed as well. The semiempirical methodology was based on the Austin model 1 Hamiltonian (AM1), while the HF SCF study was undertaken using the 6-311++G(d,p) basis set for orbital expansion. At both levels of theory, the saddle points on the potential energy hypersurfaces correspond to centrosymmetric structures, with the proton placed on the inversion center. The potential energy curves along the tunnelling coordinate were calculated by the intrinsic reaction coordinate (IRC) methodology, and the obtained energy values were subsequently fitted with analytical functions. The vibrational eigenvalues and eigenfunctions (from which the vibrational level splittings due to the tunnelling motion were calculated) were obtained diagonalising the Hamiltonian matrix within the harmonic oscillator basis.

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P9.28

INFLUENCE OF IONIC STRENGTH AND CATION NATURE ON DEPROTONATION OF METHANEDIOL STUDIED BY ^{13}C NMR SPECTROSCOPY

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In alkaline solutions dissociation of hydrated formaldehyde – methanediol occurs:

$$CH_2(OH)_2 \rightleftarrows CH_2(OH)O^- + H^+ \qquad (1).$$

The ^{13}C spectra were measured in formaldehyd solutions at the ionic strength of the electrolyte equal 0.4 and 1.0 mol/l. Due to the rapid proton exchange between methanediol and its anion a single peak of ^{13}C signal witch is weighted average of the shift of both species is observed in the spectrum. The chemical shift (δ) of the potonated form of methanediol (1) is observed at 83.0 ppm in accordance with the literature data. When analyzing the dependences of ^{13}C chemical shift of methanediol *vs.* pD it is seen, that these dependences have a typical form of titration curves from witch pK_a values were determined as the inflection point.

The results obtained show a trend of decrease in pK_a values with increase in ionic strength of the solution, *i.e.* ionic strength does not effect the rate of reaction between non-charged species (in our case the reaction of deprotonation) and decreases the rate of reaction, involving two species with opposite charges (reaction of protonation). This is in agreement with the influence of ionic strength on the reaction rate. Ionic strength effect rises in the sequence $Li^+<Na^+<K^+$, this can be related to different changes in the activity coefficients of $LiNO_3$, $NaNO_3$ and KNO_3 with concentration increase.

ACRYLAMIDE AS AGENT MODIFYING MELAMINE-ACETONE-FORMALDEHYDE RESINS

P9.29

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The purpose of the experiments presented in this paper was to obtain a new polymeric material based on acrylamide-modified melamine resins. Acrylamide was used to enhance waterproof properties of the resins.

In this article we explain the process of dissolution of acrylamide in the reactive solvent - melamine systems. The solvents used in this process are synthesized in the exhaustive reaction of 1 mole acetone with 1-12 moles of formaldehyde. The reaction of acrylamide in the reactive solvent and reaction of acrylamide in the reactive solvent - melamine system were carried out under the same conditions. The components of the reaction were mixed and progressively heated up to 105°C. During the process of acrylamide dissolution, the reaction mixture was sampled continually (at 30s intervals over a period of 3 minutes [1]). Each sample was analyzed by nuclear magnetic resonance (^{1}H-NMR) method, and the spectra were used to examine the course of the reaction. This spectroscopy technique was chosen for this experiment, as it is one of the most successful methods for investigating the structure and properties of various organic substances [2]. ^{1}H-NMR spectra were recorded by means of a BS 587A (80 MHz) spectrometer. The analysis of spectra obtained in the process led us to the conclusion that acrylamide is to a considerable degree only a physically modifying agent, and it doesn't polymerize during its dissolution. Acrylamide reacts only to small extent with formaldehyde released from the reactive solvent (a product of reaction of acetone with CH_2O in large excess), leading to the formation of hydroxymethyl derivatives. These derivatives condense with hydroxymethyl derivatives of both dissolved melamine and reactive solvent, and so they build in the structure of the analyzed system.

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P9.30

^{1}H, ^{13}C AND ^{15}N NMR STUDY OF 5-CARBOXYMETHYL-1,2,4-TRIAZOLE AND 5-OXO-1,2,4-TRIAZINE DERIVATIVES

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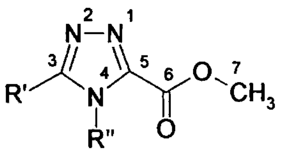
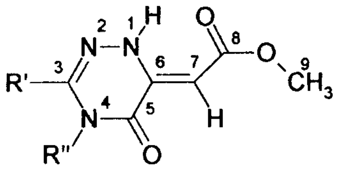
The reaction of the N^3-substituted amidrazones with dimethyl acethylenedicarboxylate led to the formation of derivatives of dimethyl 2-[(1-arylamino-1-arylmethylidene)hydrazono] succinate. In the reaction of cyclization of dimethyl 2-[(1-arylamino-1-arylmethylidene) hydrazono]succinate the compounds with six-membered ring (1,2,4-triazines) and five-membered ring (1,2,4-triazoles) derivatives are formed.

As a part of our work on the development of novel compounds with fungi- and/or bacteriostatic activity the 5-carboxymethyl-1,2,4-triazole (**1**, **2**, **3**) and 5-oxo-1,2,4-triazine (**4**, **5**, **6**) derivatives were synthesised. The structures of the studied compounds (with atom numbering) are shown in the Scheme below.



1 - 3



4 - 6

Compound	R'	R"
1, 4	C_6H_5	C_6H_5
2, 5	2-C_5H_4N	C_6H_5
3, 6	2-C_5H_4N	CH_3-C_6H_4

In order to gain further insight into the structural features, which determine biological activity, the multinuclear NMR in solution (^{1}H, ^{13}C and ^{15}N NMR including g-HSQC, g-HMBC, g-HMQC 2D techniques) and ^{13}C CPMAS NMR for solids were used. The studied compounds **1 - 6** were also examined by molecular modelling (semi-empirical, PM3).

UV-SPECTROSCOPIC AND POTENTIOMETRIC STUDIES ON PROTOLYTIC EQUILIBRIA OF DIHYDROXYANTHRAQUINONES IN NON-AQUEOUS SOLVENTS

P9.31

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Quinones are compounds of great biological importance. In the respiratory enzymes they constitute a part of electron-transfer chain. The derivatives of 9,10-antracenodione are often used in anti-cancer therapy as DNA-intercalating agents. However, their application is limited by the peroxidating properties which result in severe cardiotoxicity. It has been demonstrated in many publications that the redox properties of antraquinones are strongly connected with their acidic-basic properties. For instance, antraquinone derivatives without proton-donor groups cannot mediate electron transfer to molecular oxygen, which is the main mechanism of antraquinone-mediated peroxidation. The ability to intercalate tumor DNA also depends on the presence of hydroxy groups that are able to form hydrogen bonds with DNA bases. For the reasons mentioned above acidic dissociation (1) and anionic homoconjugation (2) equilibria in the systems of some chosen dihydroxyantraquinones were studied by means of UV-spectroscopy and potentiometric titration methods in the following polar non-aqueous solvents of various dielectric and acidic-basic properties: acetonitrile, dimethyl sulfoxide, and methanol. Apart from above equilibria, the dissociation of water (3), which even in most carefully purified non-aqueos solvents is present [1,2} at concentration about 10^{-3} M, has been considered:

$$HA + SH \rightleftarrows A^- + SH_2^+ \qquad (1)$$

$$AH + A^- \rightleftarrows AHA^- \qquad (2)$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad (3)$$

The measurements were carried out in anaerobic conditions, in order to prevent the oxidation of phenolic parts. The determined pK_a values range from about 12 -14 in dimethyl sulfoxide and methanol to 22 -24 in acetonitrile. For all compounds and all solvents studied the anionic homoconjugation equilibria are present in solution, which is confirmed by significant values of the homocongation constants. Namely, the logarithms of anionic homoconjugation constants are of the order of 2 - 3 in all solvents studied. Moreover, for polar aprotic solvents studied, protophobic acetonitrile and protophilic dimethyl sulfoxide, the observed tendency towards anionic homoconjugation is generally consistent with the order of basicity of the solvents.

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P9.32

VIBRATIONAL SPECTRA OF THE ADDUCT OF 1,8-BIS(DIMETHYLAMINO)NAPHTALENE WITH DICHLOROMALEIC ACID (DMAN·DCM)

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The infra-red (IR), Raman (R) and inelastic incoherent neutron scattering (IINS) spectra, particularly in low frequency region, of the title ionic adduct were studied. It is shown that all low frequency vibrations (below 200 cm^{-1}) of $(CH_3)_2N$ groups of protonated DMAN-clearly observed in IINS spectra-are sensitive to the environment, i.e. to the type of counterion forming short contacts with C-H bonds of methyl groups. The internal frequencies were also calculated by *ab initio* method. The results are consistent with numerous of the counteranion effect on the geometry of the protonated DMAN. The conclusions are compared with structural and NMR studies reported recently for the DMAN·DCM adduct. The single crystal Raman polarized spectra taken over the frequency range 20-3200 cm^{-1} were analyzed in detail. We have shown that substantial differences in the IR spectrum of the DCM anion in the DMAN adduct and in the potassium salt results from different geometries of OHO hydrogen bonds. In the case of potassium salt the chains of longer intermolecular hydrogen bonds are formed described by means of a double minimum potential.

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P9.33

SULFONAMIDES AS N-H ACIDES

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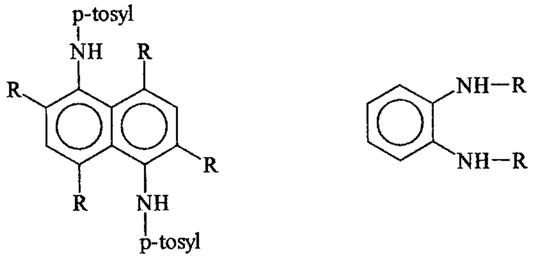
The series of 1,5-bis(p-toluenesulfonamido)-naphthalene and di-, tri- and tetra-nitro derivatives and ortho-substituted benzenes were obtained (Fig.1) The main interest in these synthesis comes from N-H acidic properties of its amides groups and is connected with studies on proton transfer of N-H acids with DMAN and other „proton sponges". The previous papers have dealt with others similar compounds: 1,8- bis(p-toluenesulfonamido)-naphthalene and nitroderivatives [1-2]. ^1H , ^{13}C NMR and IR spectroscopy are valuable metods in studing hydrogen bond behaviour in similar systems what was previously documented [3]. Titled sulfonamides and their complexes with proton sponges were studied with the aid on ^1H, ^{13}C NMR and IR spectroscopy and compared with results for 1,8- bis(p-toluenesulfonamido)-naphthalenes and X-ray structure of 1,5-bis(p-toluenesulfonamido)-2,4,6,8-tertanitronaphthalene [4].



R= NO_2 or H

R= SO_2-C_6H_4-CH_3 or SO_2-C_6H_4-CH_3

Fig. 1. Studied compounds

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P9.34

THE MULTINUCLEAR NMR STUDY OF THE INTRAMOLECULAR HYDROGEN BOND IN SCHIFF-MANNICH BASES

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Two new Schiff-Mannich bases (**1**), (**2**) with competitive proton-acceptor nitrogen atoms were synthetized (Fig. 1). The ^{1}H, ^{13}C and ^{15}N NMR spectra of compound (**1**), (**2**) were registered in $CDCl_3$ solution at variable temperature. In compound (**1**) OH group form intramolecular hydrogen bond only with N-atom of the azomethine group, conjugated with the aromatic ring. In compound (**2**), the rotation of the OH group was observed. At 230K two form with intramolecular hydrogen bond were found: to N-atom of the azomethine group and N-atom of the aminomethyl group. The lower basicity of the N-atom linked to the aromatic ring in respect to N-atom linked to the aliphatic group is responsible for different behavior of both compounds.

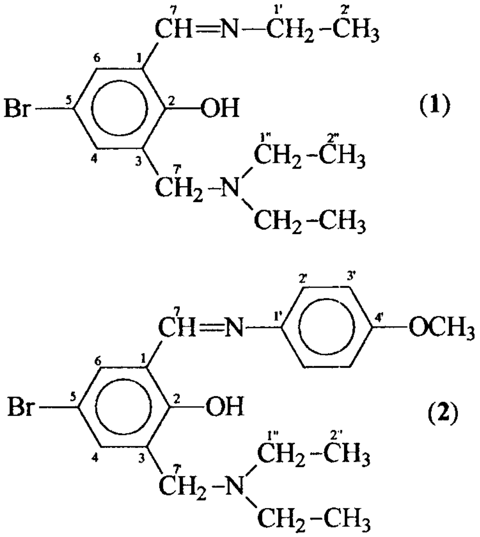

Fig.1 Studied Schiff-Mannich bases

THERMAL DECOMPOSITION OF ALIPHATIC AZIDES BY UVPES

P9.35

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Organic azides have biochemical applications (1) and they are also important industrially in, for example, seismic explosives (2), the manufacture of superconductors (3) and photoresistors (4). The mechanisms of their decompositions and the electronic states of the intermediates formed are largely unknown. Due to the intrinsic instability of these compounds their properties are difficult to measure. Control of the decompositions, either in the gas phase or in gas-surface interface is needed to characterise them in much more detail in order to improve our understanding of the reactions and to widen the range of industrial applications of organic azides.

A study of the mechanisms of these reactions is being carried out by means of ultra-violet photoelectron spectroscopy (UVPES) (5,6), mass spectrometry (MS) (7), and surface analysis techniques (SIMS and WF microscopy, AES, XPS, ISS) (8).

Results of the thermal decomposition of 2-azido-acetamide, $N_3CH_2CONH_2$, and ethyl azidoacetate, $N_3CH_2COOC_2H_5$, using ultraviolet photoelectron spectroscopy are reported. Supporting *ab initio* and density functional theory calculations of molecular structure and vibrational spectra of the parent azides (9) and their possible decomposition products will also be presented.

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P9.36

^{1}H-NMR AND ^{13}C-NMR SPECTRA OF SOME IODINE SUBSTITUTED NAPHTHOLIC SCHİFF BASES

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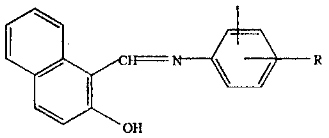
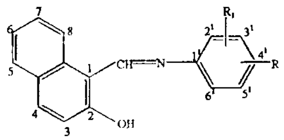
Iodoarenes are valuable synthetic intermediates in medicinal and biochemical application(1-5) Iodine is the least reactive halogene in aromatic substitution. Except for active substrates, an oxidizing agent must normally be present to oxidise I_2 to a better electrophile(6). Examples to such oxidizing agents are $(NH_4)_2S_2O_8$-$Cu(OAc)_2$(7), $(NH_4)_2S_2O_8$(8), $NOBF_4$ or $NaNO_3$(9)or the use of $(NH_4)_2Co(NO_3)_6$(10). Above reagents are succesfull for the iodination of electron rich aromatic compounds and the work up with these reagents are somewhat tedious(11,12).For the iodination of the decactivated aromatics the use of N-iodo succinimide in the presence of trilflorometanesulphonic acid has given the iodo derivatives in good yields(13).

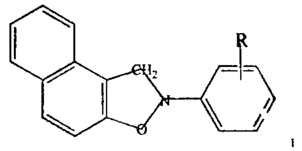
While we were trying the ring closure of some naphtholic Schiff bases (1 a ,b ,c ,d) according to method of Lokhande and Ghiya, instead of the ring closed products (3 a, b, c, d) we obtained some iodine substitiuted Schiff bases (2 a ,b, c ,d ,e).



1
a R=H; b R=2-CH$_3$
c R=3-CH$_3$; d R=4-CH$_3$



2
a R=H, R$_1$=4'-I; b R=2-CH$_3$, R$_1$=4'-I
c R=3-CH$_3$, R$_1$=4'-I; d R=3-CH$_3$, R$_1$=6'-I; e R=4-CH$_3$, R$_1$=4'-I



3
a R=H; b R=2-CH$_3$; c R=3- CH$_3$; d R= 4-CH$_3$

From their mass spectra it was found that iodine was substituted to the phenyl ring instead of ring closure (4, a, b, c, d,)

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SPECTROSCOPIC ANALYSIS OF *trans*-9-(4-CYANOSTYRYL)- -2,3,6,7-TETRAHYDRO-1H,5H-PYRIDO[3,2,1-i,j]-QUINOLINE AND ITS DEUTERIUM LABELLED ISOTOPOMERS

P9.37

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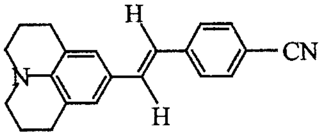
Stilbene derivative *trans*-9-(4-cyanostyryl)-2,3,6,7-tetrahydro-1H,5H-pyrido-[3,2,1-i,j]-quinoline (julolidine stilbene, JSB) and its three deuterium labelled isotopomers were prepared by the Wittig-Horner-Emmons method. Their ^{1}H and ^{13}C NMR, infrared, Raman and mass spectra were recorded and assigned.



JSB

Reaction mechanisms and problems that occurred during the synthesis of a series of deuterium labelled isotopomers were followed by a combined spectroscopic analysis. For example, in order to avoid exchange of deuterium with hydrogen in the olefinic bridge, deuterium labelled solvents should be used. The most important results relevant to "push-pull" stilbenes will be discussed.

P9.38

INFLUENCE OF Ag COLLOID AGGREGATION ON PORPHYRIN SERRS SPECTRA MONITORED VIA RAMAN CORRELATION SPECTROSCOPY

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The technique of correlation spectroscopy is based on substantial increase of the Raman signal noise caused by fluctuations of the scattered objects in the excited volume. Thus, an optical signal from sources the number of which fluctuate randomly inside the inspected volume can be distinguished by means of a statistical noise analysis [1-3]. CCD detection system enables to record entire wide spectral regions using sampling times of tenths or units of seconds. These times correspond well to the typical correlation times of solid particles levitating in the excited volume of non-stirred aqueous samples [2]. In this contribution, we demonstrate applicability of this approach to separate SERRS (Surface-enhanced resonance Raman scattering) spectra of copper(II)5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphyrin (CuTMPyP) obtained from the fluctuating large colloidal aggregates and from those of "solution" (small colloidal aggregates or single particles).

1000 SERRS spectra of borohydride-reduced Ag colloid/CuTMPyP system containing colloidal aggregates of varying size were consecutively recorded by CCD Raman instrument using a 0.5 sec exposition time. Since no bandpass filter was used, spectra contained both the porphyrin SERRS bands and the plasma lines of Ar^+ laser. Results obtained from factor analysis (FA) [4] of the spectra show two SERRS signal components, the first from porphyrins adsorbed on single colloidal particles and the second from the porphyrins in Ag aggregates. The number of aggregates inside the excited volume is several orders lower in comparison with the single particles, and due to the fluctuation of this number an increased noise of the later component is expected. This noise should correlate with the noise of the plasma lines intensities, originated in the elastic scattering and therefore being dependent in the same way on the presence of the aggregates inside the excited volume.

An evaluation of the correlation between the plasma line signal and the two FA spectral constituents obtained for the SERRS bands allowed us to construct the SERRS spectra of both SERRS-active formations. While positions of the CuTMPyP SERRS bands were obtained the same in both cases, the mutual ratios of some of them remarkably differ.

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IDENTIFICATION AND SPECTROSCOPIC PROPERTIES OF SHORT-LIVED INTERMEDIATES GENERATED UPON PHOTODEGRADATION OF PESTICIDES

P9.39

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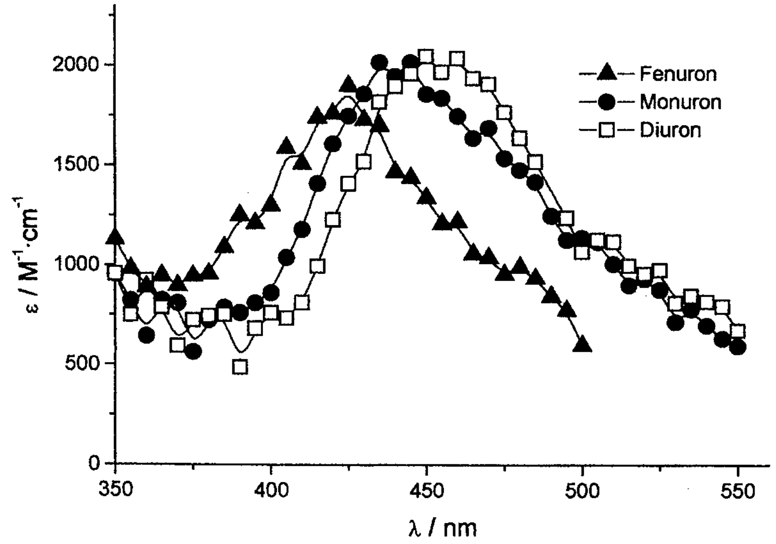
As part of a project endeavouring to clarify the photodegradation of common pesticides, we studied by time-resolved laser-flash photolysis and pulse radiolysis, with spectroscopical detection, the mechanism of generation, and the spectral and thermodynamic properties of radicals derived from different commercially available pesticides.

In general, the photodegradation involves a photoionization process, the number of photons involved depends on the photon energy (wavelength) of the exciting light. The observed photoionization quantum yields were found to be very low for all the studied compounds. These observations imply that the different studied pesticides are not photodegraded by sunlight.

In this communication we report on the spectroscopic properties of the generated intermediates, and compare the experimental results with those theoretically obtained. The figure below shows the modifications observed in the spectrum of the short-lived intermediates generated upon photolysis of substituted *N*-phenyl-(*N'*,*N'*)-dimethylurea-based herbicides when zero, one or two Cl atoms are placed on the aromatic ring.



P9.40

CHARACTERIZATION BY RAMAN SPECTROSCOPY OF POLYAMINE-INDUCED AGGREGATES OF OLIGODEOXYRIBONUCLEOTIDES

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Experimental evidence that polyamines interact with DNA has been achieved in the last years [1]. This interaction has demonstrated to be efficient on DNA protection from several agents, as reactive oxygen species or radioactivity [2]. However, the true nature of the polyamine-DNA binding, and its influence on the physiological roles of the polyamines are not clearly established.

Since several years we are focusing our attention on applying the vibrational spectroscopy to the study of this interaction. Here, we present the molecular effects of ornithine-derived polyamines (Figure 1) on a short double-stranded oligodeoxyribonucleotide in solution, using FT-Raman spectroscopy.

$NH_3^+–(CH_2)_4–NH_3^+$	putrescine
$NH_3^+–(CH_2)_4–NH_2^+–(CH_2)_3–NH_3^+$	spermidine
$NH_3^+–(CH_2)_3–NH_2^+–(CH_2)_4–NH_2^+–(CH_2)_3–NH_3^+$	spermine

Figure 1. Chemical structures of the three ornithine-derived polyamines

FT-Raman spectra of an alternating purine-pyrimidine DNA sequence with polyamines at milimolar concentrations, ranging different molar ratios, have been recorded. The interaction with G-C base pair has been studied in a 15 base complementary sequence. The Raman bands of the oligomer exhibit clear intensity decrease by augmenting the polyamine concentration (hypochromism), which has been largely attributed to base stacking and pairing [3]. This effect can be related with the double-strand packaging to an aggregated state in solution. It has been proposed that polyanions and polycations could dispose alternatively in a cholesteric arrangement where cations would have a high degree of mobility along the strands [4]. Several studies have suggested that aggregation is a prerequisite for transfection of oligonucleotides and plasmid vectors in living cells [5]. In the present work we have used Raman spectroscopy to improve our knowledge about this relevant phenomenon.

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SURFACE NANOSTRUCTURE of ZIRCONIA : FT-IR STUDY of, HYDROXYLS, ACTIVATION and METHOXYLATION

P9.41

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Tetragonal t-ZrO_2 nanosize particles were synthesized from hydrolysis of $ZrCl_4$ (670-870K) with cristallite size diameter $\varnothing \approx 20$nm, i.e. very near that observed in oxidized zircaloy plates. Monoclinic m-ZrO_2 was obtained either from an autoclave treatment (H_2O, 770K, 10^5hPa) with $\varnothing \approx 50$nm or from heating in air, $\varnothing \approx 40$nm.

Activation of pure powders under dynamic vacuum, in an in-situ cell, step by step with a 100K increment, cleans the surface from physisorbed water molecules. The characteristic band surface at ca 3360cm^{-1} gradualy decreases in intensity and at the same time the wavenumber of the maximum absorption is increased up to $\approx$3500cm^{-1}. This evolution is connected with stronger hydrogen bonds found near the surface.

Two hydroxyls (Zr_x-**O-H**) species are observed on t-ZrO_2 surface which are multiplied on autoclave treated m-ZrO_2. This structured absorption can be correlated with the different cristallographic planes displaid on the grains. Hydroxyls are identified through H / D isotopic exchange ($\approx 3700 \rightarrow 2700$cm^{-1}).

The FT-IR spectra of the methoxy groups obtained after t-ZrO_2 or m-ZrO_2 surface hydroxyls reaction with methanol

$$Zr\text{-}\mathbf{OH} + CH_3O\text{-}\mathbf{H} \rightarrow Zr\text{-}OCH_3 + \mathbf{H_2O}$$

brings up the $\nu(CH_3)$ ($\approx$ 2960-2840cm^{-1}) absorptions, so that the terminal and bridged $\nu(CO)$ respectively assigned at 1150 and 1040cm$^{-1\cdot}$ Their temperature behaviour is followed, exhibiting a progressive intensity decrease up to other products formation depending on zirconia polymorph.

Spectroscopy and Chemical Dynamics (3)

-Molecular Dynamics
-Phase Transitions
-Dynamics in Metal Atoms' Containing Systems

THEORETICAL AND EXPERIMENTAL STUDIES OF RAMAN AND XPS SPECTROSCOPIES OF MOLECULAR SYSTEMS

P10.1

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We describe a new approach to the theoretical interpretation of Raman and XPS spectra of molecular systems where complex geometry and bonding patterns can cause problems. It uses ideas from condensed-matter science, combining self-consistent quantum chemistry with molecular dynamics, rather then regarding these as successive steps. Self-consistent geometry optimisation and molecular orbital calculations have been carried out within CNDO (Complete Neglect of Differential Overlap) approximation in a cluster model framework using a modified version of the CHEMOS code [1,2].

We report here a self-consistent calculation of the vibrational frequencies of glycerol. The calculated results are compared with the experimental ones obtained by Raman spectroscopy [3]. Our theoretical results should provide qualitative information on the preferential vibrational modes of glycerol.

The possibility of using the same approach to investigate the XPS spectra of metal atoms deposited on PMDA-ODA is also discussed. In order to study the interaction of metal atoms with PMDA-ODA we have simulated the bonding of Al, Cr, Cu and Ni atoms with specific groups of PMDA-ODA. Our results suggest that metal atoms induce charge rearrangements among the PMDA-ODA atoms that lend to core level shifts far from the reaction site. Therefore, changes in XPS line profiles of the carbonyl group of PMDA-ODA cannot be associated with metal reaction at that site. Despite the fact that the absolute value of calculated core level shifts may not be correct, we believe the qualitative results to be reliable and these show important features.

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P10.2

A MOLECULAR DYNAMICS STUDY OF FULLERENE CYANOADAMANTANE MIXTURE

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We use molecular dynamics method (MD) to simulate the structural properties of cyanoadamantane ($C_{10}H_{15}CN$) molecules at fullerene (C_{60}) environment. It was simulated for two configurations of CNa molecules with anti- and ferroelectric orders of molecular axis as a function of temperature (over a range of 100-800 K).

Two models have been used in our calculations. The interactions between two C_{60} molecules have been modelled as one site, using the aproach proposed by Girifalco [1]. Cyanoadamantane molecules were represented by a rigid three-site model, using the aproach proposed by Cathiaux [2]. Fig. 1 shows the cyanoadamantane molecule, which is composed of two atomic sites C and N for cyano group and one site playing the role of entire adamantane atoms (CNa).

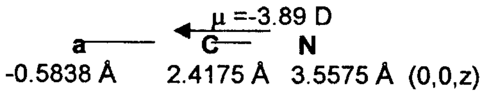

Fig.1 – Model of cyanoadamantane molecule.

The static and dynamics properties are calculated for three phases (crystalline, plastic and fluid) and compared. The structural properties of the system have been studied in terms of the radial distribution function (g(r)) as well as the order parameter (P_2). The rotational and translational dynamics of the system have been observed in terms of the autocorrelation ($C_v(t)$,$C_\omega(t)$) functions.

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A MOLECULAR DYNAMICS STUDY OF CYANOADAMANTANE DESORPTION FROM FULLERIDE MATRIX

P10.3

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We use molecular dynamics method (MD) to simulate the desorption process of cyanoadamantane ($C_{10}H_{15}CN$) molecules from fulleride (C_{60}). The escaping of CNa is studied for several densities of investigated systems as well as a function of temperature (over a range of 400-2000 K).

The structural properties of the system have been studied in terms of the radial distribution function (g(r)) and order parameter (P_2). The dynamics of the system have been studied in terms of the diffusion coefficient (D(T)) and the autocorrelation ($C_v(t)$,$C_\omega(t)$) functions.

We show that the temperature in which the system is no longer in crystalline phase strongly depends on densities of studied mixtures. All transition temperatures (crystaline, liquid and gazeous) decreased for decreasing densities of the systems.

P10.4

INFRARED AND DIELECTRIC SPECTROSCOPY STUDY OF THE WATER PERTURBATION INDUCED BY TWO SMALL ORGANIC SOLUTES

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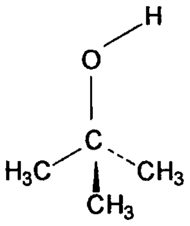
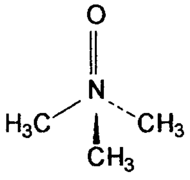
The hydration of solutes with apolar surfaces in aqueous solutions is a problem of great interest in biological systems.

This work concerns a comparison of the hydration properties of two simple molecules of biological relevance: trimethyl-amine-N-oxide (TMAO) and tert-butyl alcohol (TBA). These molecules are geometrically very similar, having the same hydrophobic moiety and different polar groups (see Figure).

Both molecules have been used as a model to study hydrophobic behaviour in water solutions.



TBA



TMAO

In the present work, dielectric relaxation of water/TBA and water/TMAO mixtures has been studied as a function of cosolvent mole fraction, X, in the water rich region of composition. Water perturbation induced by TBA and TMAO molecules has been studied also as a function of X by using the absorption bands due to the vibrational modes of water in the infrared region. The data show, in agreement with molecular dynamics simulation results [1], that TMAO and TBA interaction with water are remarkably different and that water molecules are more tightly coordinated by TMAO than by TBA. These results are consistent with the relative strengths of the electric dipole moment, being $\mu_{TMAO} \approx 3\ \mu_{TBA}$.

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REORIENTATIONAL DYNAMICS OF THE BENZENE GUEST MOLECULES IN HOFFMANN AND HOFFMANN-T_d TYPE CLATHRATES

P10.5

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The reorientational dynamics of benzene guest molecules in two series of inclusion compounds – Hoffmann and Hoffmann-T_d clathrates was studied employing FT IR and Raman spectroscopic methods and the transition dipole moment time correlation function approach.

Room and low temperature (~ 100 K) Fourier-transform infrared and Raman spectra of the Hoffmann clathrates of general formula $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ (where $M \in \{Ni, Co, Cd, Fe, Mn, Mg, Zn\}$ while $M' \in \{Ni, Pd, Pt\}$) and Hoffmann-T_d clathrates $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ (where $M \in \{Zn, Mn, Hg, Cd\}$ and $M' \in \{Cd, Hg\}$) were recorded. Special emphasize was placed on the out-of-plane CH bending modes of enclathrated benzene molecules, which were shown to be the only spectroscopic indicators of the host-guest interactions within the mentioned systems.

The transition dipole moment time correlation functions of the □(CH) modes were obtained by Fourier inversion of the corresponding IR and Raman bands. From the obtained time correlation functions, conclusions regarding the reorientational dynamics of the enclathrated species, as well as of the vibrational relaxation of the studied modes were derived. The reorientational correlation times were calculated and correlated with the unit-cell volumes of the host matrices. The average angles of "free rotation" were estimated, together with the mean squared torques. The obtained results further support the theoretical concept according to which the short-range repulsive forces in the host matrix are responsible for inducing relaxation.

P10.6

CORRELATION BETWEEN PHASE TRANSITION AND VIBRATIONAL DYNAMICS OF DIPHENYLACETYLENE IN LIQUID SOLUTIONS AND SOLID STATE, AND LIQUID – SOLID B, SOLID B – SOLID A ACETONITRILE TRANSITIONS IN THE 77K – 293K RANGE

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Diphenylacetylene (DPA) is particulary interesting because it offers a wide range of electronic structures going from the ground S_0 to T_1, radical ions $DPA^{+\bullet}$ and $DPA^{-\bullet}$. Some of phenylacetylene are of particular interest with regard to the most recent liquid crystal technology, namely, polymer dispersed liquid crystals (PDLCs). The PDLC technology uses fluorinated diphenylacetylene to achive high–purity nematic materials [1]. The ealier research performed in our laboratory [2] concerned on phenylacetylene derivatives and diphenylacetylene in the liquid and solid phase. We will presend Raman spectra of the ν_s (C≡C) stretching mode of the diphenylacetylene (DPA) dissolved in acetonitrile, benzene and metylcyclohexane have been recorded in liquid solutions at room temperature and in solid state frozen matrices as a function of concentration and of temperature. The spectra at low temperature reveal a spectacular changes in comparison with those observed in liquid solutions. The results illustrate the change of the mechanisms of vibrational relaxation due to structural reorganizations around the molecular oscillator due to different molecular environments. Raman technique is very sensitive, to change in intermolecular structure that accompany transitions from isotopic liquid phase through liquid crystalline phases with increasingly higher positional order to the crystalline solid. These structural changes are reflected in frequency shift and sometimes drastic changes in intensities and linewidths of vibrational bands. Because a lot of aspects of the Raman and IR spectra of diphenylacetylene derivatives are not well understood we performed further measurments in the broad temperature range from 77K to 293K for isotopic mixtures with deuterated substitutents. The isotopic effect helped to determine if the proposed so far explanations of our result are right. We will also present the band shapes in isotopic mixtures of acetonitrile as a function of composition. The effectiveness of isotopic mixture crystal studies for determining the nature of the splitting is very important because the multiplet structure due to the Davydov effect in neat crystals is perturbed sevely by isotopic substitution. We will present the results the Raman Spectra of the internal vibrational modes: ν_5 (E), ν_1 (A_1), ν_6 (E), ν_2 (A_1) ν_3 (A_1), ν_7 (E), ν_1 (A_1), ν_8 (E) and the lattice region of 15-200cm^{-1} of acetonitrile as a function of temperature in the 77K-293K range [3]. We will show that the liquid – solid β phase and solid β – solid α transitions are accompanied by marked changes in the Raman spectra. The aim of the present study is to obtain information about the nature β→α transition in acetonitrile and to give a contribution for understanding the correlation between the mechanism of the phase transitions, vibrational dynamics and static properties of the internal and external lattice modes.

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THE VIBRATIONAL SPECTROSCOPY OF THE INTERACTIONS AND DYNAMICS OF PARTICLES IN LIQUIDS AND SOLUTIONS

P10.7

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The properties of the solution and the kinetics of the physical and chemical processes taking place in it are largely determined by the singularities of the interactions and the dynamics of the constituent particles.

In investigation of interactions and dynamics of polyatomic particles the prominent part is played by the vibrational spectroscopy methods.

Interactions between molecules and ions disclose themselves in the changes of the number of the observed bands, the discrete shifts of the maximum positions, the increase of decrease in integral intensities. Analyzing these changes, one can obtain detailed information on the structure of the forming complexes and associates and also reveal the atoms responsible for these interactions, the character of coordination, the nature of interparticle coupling. The character of intramolecular vibrational and Brownian orientational motion of molecules and polyatomic ions makes itself manifest in the band contour shapes of infrared absorption and Raman scattering of light. The method of time correlation functions, which play the role comparable to that of distribution functions in statistical physics and are derived by the Fourier transformation of the observed contour, allows one to follow the molecular dynamics at length.

Raman spectroscopy has a certain advantage here. Polarization measurements allow the separation of that part of the total band spectrum which is associated only with the rotational molecular motion or only with the processes of the intramolecular vibrational energy dissipation to the outer degrees of freedom. Studying vibrations with different types of symmetry one can judge upon the mechanism of rotation of the particle and evaluate the times of relaxation and the angles of rotational turns.

In the IR absorption band contour, it is impossible to separate the purely rotational contribution from the dissipational one. The peculiarities of the rotational motion of polyatomic particles can be studied by comparative investigation of the IR and Raman bandshapes of the same vibration.

The examples are given of studying vibrational and orientational relaxation of molecules and polyatomic ions and the influence exerted upon them by various interparticle interactions occuring in solutions of different nature.

P10.8

SERS-ACTIVATION OF SMOOTH SURFACES BY DOPING WITH SILVER NANOPARTICLES

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Raman spectra of organic ligands adsorbed on non SERS-active substrates can be easily obtained by deposition of silver colloidal particles onto smooth surfaces with adhering adsorbate [1]. The SERS-activation derives from the electromagnetic enhancement assured by the silver particles. For these experiments 2,2'-bipyridine has been used as ligand, because it strongly adsorbs on metals, giving rise to different adsorbates. Scanning electron microscopy (SEM) and UV-visible extinction spectroscopy have been employed to study the morphology of the surfaces. The deposited silver layer consists of a quite uniform distribution of non aggregated nanoparticles with 20-30 nm as average diameter.

This activation procedure is efficient for obtaining SERS spectra of ligands adsorbed on smooth metals, like Cu, Au, Ag, Al, Ni, as well as for non metal substrates, like Si, Ge and quartz. In the case of nickel, whose low optical reflectivity prevents electromagnetic Raman enhancement, a very strong SERS spectrum has been detected. In this case the electromagnetic enhancement factor results about 1000, in agreement with previous theoretical and experimental findings [2].

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METAL-AMMONIA INTERACTIONS: OPTICAL SPECTROSCOPY OF YTTRIUM IMIDE AND THE ALUMINUM-AMMONIA COMPLEX

P10.9

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Complexations and oxidative additions at metal centers are very important classes of reactions in homogeneous catalysis. Two examples will be reviewed and discussed: Y + NH_3 and Al + NH_3. The reaction of yttrium with ammonia proceeds without formation of a stable adduct. The N-H bond is readily activated and the reaction proceeds with the elimination of molecular hydrogen to produce yttrium imide, YNH(D). We have studied the visible spectrum of yttrium imide using laser-induced fluorescence and photoionization spectroscopy. Following a brief survey of the visible spectrum, the presentation will focus on the origin bands of the $\tilde{B}^2\Sigma^+ - \tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi - \tilde{X}^2\Sigma^+$ systems for which rotational, fine and nuclear magnetic hyperfine structures have been analyzed in detail. Dipole moments, ionization potential and binding energies, which have also been measured or derived, will also be discussed. The reaction of aluminum with ammonia proceeds with the formation of a stable adduct, $Al(NH_3)$, which we have studied using photoionization spectroscopy. Resonant two-photon ionization (R2PI) yielded a vibronically resolved spectrum in the 18000-21000 cm^{-1}, which is believed to be due to four electronic band systems. Preliminary rotational analyses of some vibronic bands will be presented. Photoionization efficiency (PIE) spectroscopy yielded Rydberg spectra whose limits provide information on the ground state of the cation. All of these observations will be presented and discussed.

P10.10

VIBRATIONAL AND MÖSSBAUER SPECTRA OF $M_n(Fe(CN)_5NO)_m$ COMPLEXES ($M=Sc^{III}, Y^{III}, La^{III}, Fe^{II}$) A NORMAL COORDINATE TREATEMENT

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We explore in this study the influence of the outer sphere cations (Sc, Y, La, Fe) on the position and intensity of the $[Fe(CN)_5NO]^{2-}$ vibrational bands as well as on the Mössbauer parameters. We have measured for these complexes in the ground state far- and mid-infrared spectra at room temperature as well as Mössbauer spectra. The results are juxtaposed to existing experiments with $Na_2[Fe(CN)_5NO].2H_2O$. Our findings are explained by the obtained force constants from normal coordinate analysis (NCA) and the results from the gradient-corrected density functional B3LYP electronic structure calculations.

The second coordination sphere (Sc, Y, La, Fe) do not affect the position and intensity of the ν Fe-N as well as the δ Fe-N-O vibrations. Similarily, the Mössbauer parameters δ (isomer shift) and ΔE_q (quadrupole splitting), derived from the spectra, show no changes. The lack of impact on these vibrations are explained by the remote position of the outer sphere cation. The same applies to the Mössbauer parameters which reflect features in the electronic structure of the central iron ion.

By contrast, Sc, Y, La, Fe have a recognizeable influence on the following vibration bands. For the valence $C\text{-}N_{eq}$ and $C\text{-}N_{ax}$ vibrations there is an up shift of 20 cm^{-1} from the spectra obtained in the case of $Na_2[Fe(CN)_5NO].2H_2O$. The intensity of these bands increases in the row Na, Fe, Sc, Y, La. These two phenomena can be explained by the extraction of a π^* C-N antibonding electron density by the outer sphere cation. The results are in agreement with the calculated force constants by NCA as well as the determined charges and bond populations carried out with B3LYP method. Moreover, the ν M-N vibrations (M=Sc, Y, La, Fe) show an up shift of more than 40 cm^{-1} compared to ν Na-N. The strength of the M-N bond also causes an up shift of 20-25 cm^{-1} of the δ $Fe\text{-}C\text{-}N_{eq}$ and δ $Fe\text{-}C\text{-}N_{ax}$ vibrations. The strongest is the up shift in the case of Sc due to the small ionic radius of this cation (Fig.1). All these changes are the result of both the kinematic and dynamic interactions.

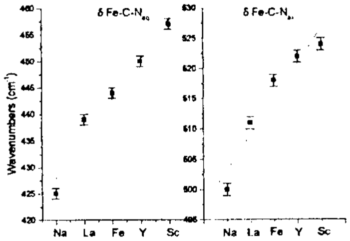

Fig.1 - The up shift of δ $Fe\text{-}C\text{-}N_{eq,ax}$ vibrations caused by the outer sphere cation

Cu(II) COMPLEX FORMATION WITH POLYAMINEPOLYCARBOXYLATES IN ALKALINE SOLUTION STUDIED BY VIS-SPECTROPHOTOMETRY

P10.11

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The Cu(II) complexes formation with *CDTA* (trans-cycloxexane-1,2-diaminetetraacetic acid), *HEDTA* (hydroxyethylenediaminetriacetic acid), *TTHA* (triethyleneteraaminehexaacetic acid) and *EGTA* (ehylenedi-oxydiethylenediaminetetraacetic acid) in alkaline solutions has been studied by VIS-spectrophotometry at 20 °C and ionic strength of solutions 3 mol/l.

The results obtained show, that Cu(II) ions form with all investigated polyaminepolycarboxylic acids $\mathrm{Cu}L^{n-}$ type complexes in neutral and weakly alkaline solutions. In alkaline and strongly alkaline solutions Cu(II) forms hydroxycomplexes with *CDTA* and *HEDTA*, and dihydroxycomplex with *TTHA* form. The logarithms of the equilibrium constants of the hydroxycomplexes formations reactions:

$$\mathrm{Cu}CDTA^{2-} + \mathrm{OH}^- \rightleftarrows \mathrm{Cu}CDTA(\mathrm{OH})^{3-} \quad (1),$$

$$\mathrm{Cu}HEDTA^{-} + \mathrm{OH}^- \rightleftarrows \mathrm{Cu}HEDTA(\mathrm{OH})^{2-} \quad (2),$$

$$\mathrm{Cu}TTHA^{4-} + 2\mathrm{OH}^- \rightleftarrows \mathrm{Cu}TTHA(\mathrm{OH})_2^{6-} \quad (3)$$

were found to be 1.5 ± 0.3, 0.8 ± 0.1 and 6.2 ± 0.4, respectively. With the further increase of the solution alkalinity (to 3 mol/l NaOH) the hydroxycomplexes decompose and transform to $\mathrm{Cu(OH)}_4^{2-}$.

In the case of *EGTA* only a $\mathrm{Cu}L^{n-}$ type complex was detected, witch with the rise of the alkalinity transforms directly to $\mathrm{Cu(OH)}_4^{2-}$ without the hydroxycomplex formation.

P10.12

STUDY OF INTERACTION OF TETRASULFONATED ALUMINUM PHTHALOCYANINE WITH HUMAN SERUM ALBUMIN

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Photosens is a promising photosensitiser based on a mixture of di-, tri- and tetra-sulfonated aluminum phthalocyanines ($AlPcS_n$, n=2, 3, 4, respectively) [1]. To clarify the role of particular components in the overall photodynamic effect induced by photosens the $AlPcS_2$, $AlPcS_3$, and $AlPcS_4$ components were separated, and their accumulation and distribution were studied in tumour cells and tissues. It was found that $AlPcS_4$ penetrates poorly into cancer cells, but accumulates selectively in connective tissue that surrounds tumour cells [2]. In this work, the binding of $AlPcS_4$ to human serum albumin (HSA) was investigated in order to clarify the peculiarities of $AlPcS_4$ transport in the circulatory system.

The characteristic changes in the long-wavelength absorption band of $AlPcS_4$ that occurred upon addition of HSA, were used to follow an the $AlPcS_4$-HSA interaction. Partially overlapped absorption spectra of free and bound ligands were deconvolved into the components, and the extent of $AlPcS_4$ binding was determined in this manner. Binding data have been analysed according to the Scatchard model. The results suggest that two binding sites of $AlPcS_4$ are present on HSA. The binding constants for the primary and secondary sites were measured to be $(3.0\pm0.1)\times10^6$ M^{-1} and $(6.3\pm0.4)\times10^4$ M^{-1}, respectively.

A competitive binding of well-studied HSA ligands was used to identify a primary binding site of $AlPcS_4$. Excess of warfarin (IIA subdomain ligand), azido-3'-deoxythymidine and L-tryptophan (IIIA subdomain ligands) did not affect the interaction of $AlPcS_4$ with the protein. $AlPcS_4$ was found to be competitively displaced by haemin. It was concluded that the primary binding site of $AlPcS_4$ is located in the subdomain I of HSA.

A high binding affinity and an abundance of the protein in blood plasma indicate that HSA can be considered as a main endogenous carrier of $AlPcS_4$.

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TEMPERATURE-DEPENDENT FAR FT-IR SPECTROSCOPY OF SPIN-CROSSOVER COMPLEXES

P10.13

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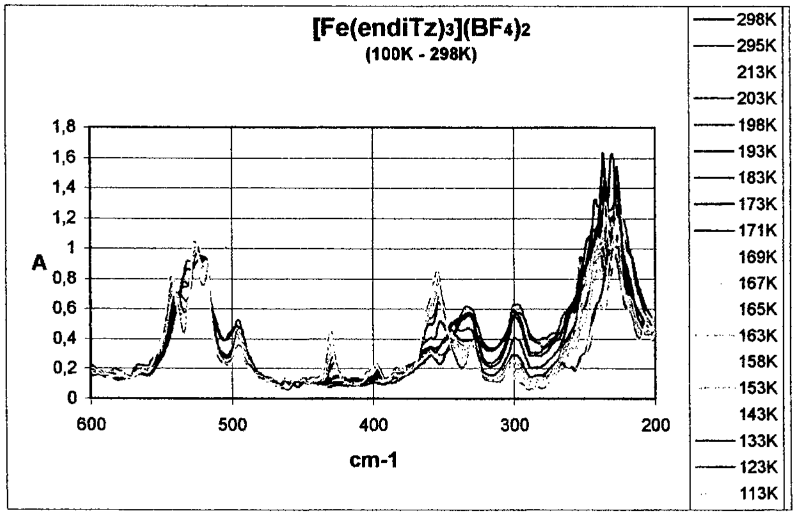
In analogy to a common synthesis of N-substituted 5-H tetrazoles, the new bidentate ligand 1,1'-(1,2-ethanediyl)bis-5H-tetrazole [endi] was synthesized, and characterized by X-ray diffraction, NMR, FT-IR and UV-VIS spectroscopy. By using iron(II) bis-tetrafluoroborate hexahydrate the complexation yields a 1-dimensional linear coordination polymer exhibiting a temperature depending spin crossover phenomenon. The thermally induced spin state switching of the iron(II) coordination center changes the energy of the d-d transition, which can be observed as a temperature dependent color change of the complex being monitored in the UV-VIS. Even more sensitive to the change of the spin state is the Iron-Nitrogen bond. The stretching vibration of the iron-nitrogen bond in the high spin complex is observed at 300 cm^{-1}, whereas the corresponding low spin complex features two absorptions at 400 and 430 cm^{-1}. The temperature depedendent data derived from far FTIR spectroscopic measurements are in good agreemnet with results, which were independently determined by temperature dependent ^{57}Fe-Mössbauer spectroscopy and temperature dependent magnetic susceptibility measurements.



Biospectroscopy (1)

-Proteins and Enzymes
-Nucleic Acids
-Sugars and Lipids

SECONDARY STRUCTURAL ANALYSIS OF CHLORAMPHENICOL ACETTYLTRANSFERASE TYPE I USING FT-IR SPECTROSCOPY

P11.1

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The growing number of enzymes, proteins and polypeptides analyzed by techniques like X-ray diffraction, nuclear magnetic resonance (NMR), circular dichroism (CD), and Fourier transform infrared spectroscopy (FT-IR) over the last decade has significantly improved and enhanced the ability to understand important correlations between bioactivity and secondary structure. One analytical method which has been steadily evolving has been FT-IR. This method has as its prime advantage the ability to rapidly acquire high signal-to-noise spectra, particularly in situations where single crystals (for X-ray) are unavailable or the complex NMR assignments have not been worked out. For instance, CD is quite sensitive to the presence of α-helices but is sometimes unable to definitely identify turns or certain β-structures due to inherently weak signals. On the other hand, FT-IR is capable of distinguishing numerous types of β-structures and turns.

Chloramphenicol acetyltransferase (CAT) [EC 2.3.1.28] is an enzyme responsible for the bacterial resistance to chloramphenicol and is therefore a subject of interest in the field of microbial ecology and molecular genetics. Among CAT family members, the type I enzyme (variant), coded by transposon Tn9, has gained much interest. The enzyme possesses some properties which are not observed in all other known CAT variants.

The secondary structure of CAT I has been studied by FT-IR and computational prediction methods. The spectral analysis of the amide I band of different samples of CAT I (KBr, hydrated films and solution) was performed using Fourier self-deconvolution method, followed by a curve fitting. The input parameters for curve fitting was investigated. The spectroscopic data provide an estimation of the α-helix and β-structure content, which depends strongly on protein sample preparation. A study of CAT I - Crystal Violet complex was performed and some changes in the secondary structure content have been detected.

The secondary structure predictions, obtained using different computational methods are well related to the FT-IR experimental data.

Taken together, these results clearly reveal that chloramphenicol acetyltransferase type I adopt an $\alpha + \beta$ fold.

P11.2

DYNAMIC LIGHT SCATTERING FROM LYSOZYME IN WATER-ALCOHOL MIXTURES

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The technique of intensity photon correlation spectroscopy has been utilised to investigate the native conformation of lysozyme in water/ethanol and in water/tert-butanol mixtures as a function of alcohol concentration in the water-rich region of composition (cosolvent mole fraction $x<0.08$). A non-trivial behaviour of the hydrodynamic radius is obtained, characterised by a minimum at $x=0.02$ and a maximum at $x=0.06$ in water/ethanol mixtures and a minimum at $x=0.005$ and a maximum at $x=0.02$ in water/tert-butanol mixtures. These values of x are close to those at which structural changes in the mixtures occur as inferred from compressibility and infrared absorption measurements. The results are discussed in connection to the effect of alcohol in modulating solvent-mediated interactions.

SITE-SELECTIVE SPECTROSCOPY OF IRON STRESS PIGMENT-PROTEIN CP34

P11.3

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The synthesis of supplementary chlorophyll-binding proteins is a common response of various microorganisms to environmental stress. The cyanobacteria Synechococcus elongatus grown under the lack of iron produces the protein called CP 34 which is generally considered to act as auxiliary light harvesting complex in primary photosynthetic processes.

A study of vibrations, electron-phonon coupling and excited energy transfer in CP 34 was based on systematic measurements of low temperature site selection fluorescence spectra. The spectral data obtained under non-selective blue excitation (into B absorption band of chlorophyll a) were compared to selectively red laser excited (into Qy absorption band of chlorophyll a) ones. The frequencies of normal vibrations [1] were determined from site selection spectra excited at different wavelengths between 660 - 690 nm. The frequencies of normal vibrations obtained in CP 34 were compared to those observed in chlorophyll-protein complexes of reaction centrum of photosystem II [2, 3].

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P11.4

SURFACE-ENHANCED RESONANCE RAMAN AND RESONANCE RAMAN SPECTROSCOPIC STUDIES OF CYTOCHROME C"

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Cytochrome c" (cyt c"), from Methylophilus methylotrophus, is a monoheme protein. Although its physiological role has not yet been firmly established, it is known that it is able to couple electron and proton transfer in the physiological pH range through a mechanism involving reversible change of the iron coordination. Despite some recent progress, many structural aspects of this protein remain unknown and up to now, no X-ray data are available. In this context, resonance Raman (RR) spectroscopic techniques constitute a promising approach for studying of the heme pocket structure.

The RR spectra of cyt c" in solution reveal that in the oxidized form the heme group is in a six coordinated low spin (6cLS) configuration, while it is in a five coordinated high spin (5cHS) configuration in the reduced state. These results confirm that cyt c" displays a redox-linked spin state transition, with two histidines (His53 and His95) as axial ligands in the oxidized form and a single histidine in the reduced form (1).

In this work, the heme pocket structure and the electron-transfer properties of cyt c" adsorbed on a silver electrode were studied by surface-enhanced resonance Raman (SERR) and resonance Raman. Potential-dependent SERR studies reveal two conformational states of the adsorbed protein in the oxidized form that prevail at potentials higher than redox potential (–0.3 v, vs. saturated calomel electrode). Whereas the SERR spectrum of one state is identical to the RR spectrum of ferric cyt c" in solution the second state displays a vibrational band pattern characteristic of a 5cHS state, indicating the loss of one of the histidine ligands. Upon further lowering the potential below –0.3 v, both species are reduced to a 5cHS state which, however, was found to degrade irreversibily as indicating by the loss of the SERR intensity.This irreversible reduction of cyt c" can be attributed to the concomitant disruption of the S-S bridge between Cys96 and Cys104 (2), closed to the heme pocket. Two experimental observations strongly support this hypothesis: (a) irreversible changes are observed when the electrode potential approach the redox potential of the S-S bridges (ca. –0.2 V); (b) upon chemical reduction of the S-S bridges with DTT, the RR spectrum of cyt c" in solution is similar to the SERR spectrum at very negative potentials. This suggests that there is a tight coupling between the heme and disulfide bridge reduction which might also be of relevance for the biological electron transfer process.

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STRATEGIES FOR THE SPECTROSCOPIC CHARACTERIZATION OF IRRADIATED PROTEINS AND OTHER BIOMOLECULES

P11.5

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The radiation damage (X-ray, UV light) of many low-molecular and macro-molecular compounds and fluids of biological and medical interest has been investigated by various physicochemical methods. In particular, spectroscopic studies of many proteins, polysaccharides, and components of the vertebrate eye, revealed, effectively and very fast, numerous changes of the local and global structure of the constituents under analysis, together with alterations of their functional ability [1-3].

In the case of irradiated proteins, UV-Vis absorption, fluorescence excitation and emission, near- and far-UV circular dichroism show changes/destruction of the constituent aromatic chromophores/fluorophores, formation of new chromophores (e.g., bityrosines), alterations of the secondary structure (helix content), exposure of initially buried (hydrophobic) groups, occurrence of partial unfolding, and pronounced aggregation (light scattering phenomena). Measurements of enzyme activity allow statements on the extent of inactivation, the effects still intensified in the post-irradiation period. Size-exclusion chromatography and analytical ultracentrifugation, coupled to fluorescence or absorption detection methods, monitor changes of the overall structure of proteins. The investigation of irradiated polysaccharides reveals similar radiation damages, though their low absorbances lead to less detailed results.

By means of various measures and additives, manifold modifications of the impact of ionizing and nonionizing radiation can be achieved. Caused by differences in the primary reactions, biopolymers are protected effectively by typical $^{\cdot}$OH scav-engers against X-irradiation, whereas compounds exhibiting significant absorption behavior in the UV range („chemical filters"), and, in some cases, also the $O_2^{\cdot-}$ scav-enger SOD, turn out to act as potent protectives against UV light. A few substances provide protection against both sorts of radiation and are even able to provide a chemical repair of already damaged particles. To allow quantitative comparisons of the damages monitored by different techniques, on the one hand, and of the protective and/or repair capabilities of different additives, on the other, appropriate evaluation, correlation and normalization procedures had to be established.

The results obtained are of importance for understanding and avoiding pathological alterations of biomolecules and for developing new strategies for protection and repair of these components (e.g., in context with aging of bio-molecules, bioprotection of eyes and skin, irradiation of food). However, the findings are also of interest for all investigators using X-rays or UV light to avoid unwanted radiation damages of their samples during the time of the experiments.

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P11.6

DIELECTRIC SPECTROSCOPY TO PROBE THE STABILITY OF THE 'KERNEL' IN RIBOSOMAL CORES

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In this communication we present an investigation on ribosomal cores, *i.e.* ribosomes deprived of select proteins by LiCl treatment. This study was done by dielectric spectroscopy. The typical dielectric behavior of the normal ribosome at radiofrequency range, consists in two subsequent relaxations that were attributed to two different organizational levels (1). This interpretation was supported by calorimetric measurements that showed two distinctive transitions (2).

Increasing concentrations of LiCl were used. Dielectric results evidenced that treatments of ribosomes with LiCl concentrations up to 2 M, affected only the first level of structural organization. To explore the effect of higher salt concentrations on the second dispersion, we treated ribosomes with LiCl concentrations up to 4.0 M. At the highest concentration a dramatic structural alteration, indicative of extensive denaturation of the particle, was evidenced. Our interpretation is that a very stable "kernel" exists. Major particle rearrangements however occur in the proximity of 2 M LiCl. This concentration is critical in the sense that relatively low concentrations do not affect the second dielectric dispersion. On the contrary slightly higher concentrations induce significant structural modifications. In conclusion it is possible to eliminate proteins without abolishing the basic structural properties of the ribosome even though this is biologically no longer functional.

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DELAY OF HEMOGLOBIN DENATURATION IN THE STATIC MAGNETIC FIELD.

P11.7

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The effect of static magnetic field (1300 G) on the stability of hemoglobin aqueous solutions was studied.

Hemoglobin (Hb) solutions with concentrations: 0.25, 0.5, 1 mg/ml were prepared from lyophilised bovine hemoglobin (produced by two different firm: "Biomed" and "Sigma") and methemoglobin (from "Sigma"). The absorption spectra were measured in the wavelength range 190 – 700 nm by using a double – beam UV VIS spectrophotometer JASCO V-530. The percentage content of Hb derivatives: methemoglobin, oxyhemoglobin, carboxyhemoglobin and sulfhemoglobin in studied Hb solutions was determined using multi – component spectrophotometric method [1].

We have examined the influence of storage circumstances on degeneration of hemoglobin solutions. By examination of UV VIS spectra details we compared the ageing of the samples kept: 1) in the refrigerator at about 4^0C, 2) at room temperature (about 24^0C), 3) in static magnetic field at room temperature.

Our results suggest that the rates of denaturation were lower when the samples were kept at low temperature or in static magnetic field. The most diluted Hb solutions changed fastest. The static magnetic field delayed denaturation of hemoglobin solutions more if the percentage content of methemoglobin was smaller.

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P11.8

BINDING OF ADENINE DERIVATIVES TO SERUM ALBUMIN

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From a pharmacological point of view it has been emphasized that the distribution of the drug in various body fluids is strongly dependent on the extent of their binding by proteins. It is possible to apply a spectrofluorimetric analysis to the binding data and thereby to correlate the energy of binding with structural features in the drug.

In this work we tried to estimate the binding constants of several adenine and adenosine derivatives to the transporting protein - bovine serum albumin (BSA). We investigated the influence of the adenine derivatives on fluorescence of the BSA tryptophanyl groups.

To point at the role of aliphatic groups in bounding to BSA we found the dependence of adenine derivatives concentration on the relative fluorescence of BSA. When ligand was bound to BSA, the fluorescence of BSA was quenched to 50% of the original value for the non-methylated derivatives and to 20% for the methylated ones.

The amount of bound ligand was calculated from the decrease of BSA fluorescence due to the binding of ligand. The binding constants were determined at 20°C and calculated from Stern-Volmer equation [1] from plots of relative fluorescence versus ligand concentration. Within the range of the concentration studied, the data under various conditions could be presented by a straight line.

The binding of the aliphatic derivatives of adenine to a single site on BSA on the contrary to non-alphatic adenine derivartives who bind also to other sites on BSA, results in a large increase in the fluorescence quantum yield of the ligand, and a slight red-shift of the fluorescence emission spectrum.

This observation suggests that the BSA binding site for aliphatic derivatives of adenine is located in a hydrophobic region of protein. This conclusion is in good correlation with our NMR study on the interactions between derivatives of the purine bases and the protein [2].

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TEMPERATURE EFFECT ON BINDING OF ADENINE DERIVATIVES TO SERUM ALBUMIN

P11.9

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The aim of this investigation was to study the release bahaviour of heat-destabilized albumin with entrapped adenine, adenosine and their derivatives in vitro

In the present work the thermodynamics and the mechanism of complex formation between serum albumin and alkil derivatives of adenine are studied by spectrofluorimetric technique.

To examine the effect of temperature on the binding of alkil derivatives of adenine to BSA and to calculate the termodynamic functions of enthalpy (ΔH) and entropy (ΔS) for the binding process, the binding constants were dermined at 20, 35, 40 and 60°C from Stern - Volmer equation. Each mixture of ligand and BSA of various molar ratio was conditioned in a constant temperature water-bath.

Analysis of the thermal destabilization data yielded dissociation constant values of 1.5×10^{-3} [M] for adenine-BSA complex and 2.0×10^{-4} [M] for alkil derivatives-BSA complexes.

Measurement of adenine fluorescence quenching of the adenine-BSA complex at higher temperature has revealed that the binding constant of the system is reduced by a factor of 2.2 at 60°C. The fluorescent quenching properties of adenine derivatives suggest that binding site of ligand to BSA was destabilized during the heating. The observation that serum albumin does not lose completely its binding properties even at temperature of 60°C was studied by NMR technique [1]

Temperature seems to induce a conformational change of serum albumin by which a ligand is surrounded by hydrophobic amino acid residues.

In the study a small negative enthalpy and a large positive entropy change have been observed.

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P11.10

FLUORESCENCE STUDY OF BINDING OF ADENINE DERIVATIVES TO THE PHOSPHOLIPIDE MEMBRANES: EFFECT OF SERUM ALBUMIN

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Several years ago a new class of drugs was described - antiviral agents - acyclic nucleoside phosphonates of purine bases (adenine, guanine, 2,6-diaminopurine) [1,2]. Freqently, the incorporation of a drug into liposomes leads to a reduced toxicity. We tried to encapsulated the model adenosine derivatives in liposome vesicles. Liposomes stability depends on several parameters: properties of the drug, size, homogeneity and a type of lipid, liposome preparation method and pH.

We applied liposomes from soy-bean lecithin (EPICURON 145V-Lucas Mayer) and cholesterol.

To increase stability against serum albumin and to minimize permeability increases caused by interaction with serum albumin, two types of liposomes consisting of various molar ratio lecithin: cholesterol were prepared. The adenine derivatives were encapsulated in liposome vesicles of two size: 100 and 450 nm, prepared by modified reverse - phase evaporation method [3].

Stability of liposomes depended on the presence of serum albumin [3] was studied by use of spectrofluorimetric technique.

To investigate the binding of adenosine derivatives to serum albumin we estimated the effect of ligand concentration on extent of quenching of tryptophanyl groups fluorescence.

In the presence of serum albumin the studied ligands encapsulated into various types of liposome vesicles were release and it results in a decrease in the fluorescence spectrum of serum albumin in the region of tryptophan emmision.

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FT-IR STUDY OF THE NATURE OF H^+ AND MONOVALENT CATIONS MOTION IN THE ION CHANNELS FORMED BY GRAMICIDIN A

P11.11

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Pentadecapeptide, gramicidin A (gA) from *Bacillus brevis* is widely used as active agent against various gram-positive micro-organisms, gram negative cocci and a large number of fungi species. GA forms cation conductive transmembrane channels which are selective to the transport of H^+ and other monovalent cations.

Gramicidin A as well as its proton, Li^+, Na^+, K^+, Rb^+, and Cs^+ complexes were studied by FT-IR spectroscopy since the ion motions are well evidenced by continuous absorption, that of proton motions in medium infrared while that of cation in the far infrared.

With increasing concentration of hydrated and protonated channels, the infrared continuous absorption increases, thus proving large proton polarizability to be due to very fast collective fluctuations and shifts of the excess proton in hydrogen-bonded single file water chain in the gramicidin channels.

The infrared spectra of the hydrated K^+, Na^+ and Li^+ cations in the gA channels show continua in the far infrared region, in the case of K^+- 140-70 cm^{-1}, for Na^+- 200-20 $cm^{-1}$and for Li^+ -400 -50 cm^{-1}. These continua are explained in terms of K^+, Na^+ and Li^+ ion fluctuations and shifts between the electron lone pairs of two water molecules as well at least three carbonyl O atoms of the backbone. The mechanism for the occurrence of the cation polarizability is the same for Li^+-gA and Na^+-gA complexes although the molecular weights and radiuses of the ions differ significantly. In the Spectra of, Rb^+, and Cs^+ complexes of gramicidin A only broad bands in the FAR infrared region are found. These bands are slightly shifted toward smaller wavenubers when compared with the corresponding ion motion bands.

P11.12

PROBING THE DYNAMIC STRUCTURE OF α-CHYMOTRYPSIN IN REVERSE MICELLES OF AOT WITH STEADY STATE AND TRANSIENT STATE FLUORESCENCE SPECTROSCOPY

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In living cells, many enzymes are located at the surface or within biological membranes. Systems like reverse micelles can provide a suitable environment to mimetize, *in vitro*, such conditions. α-Chymotrypsin, α-*Chym*, is a particularly interesting enzyme since it has been reported to exhibit superactivity in systems like the most thoroughly studied AOT/*iso*-octane/water reverse micelles. The physicochemical properties of water solubilised in this system at low ω_o, $\omega_o=[H_2O]/[AOT]$, are rather different from those of bulk water. An attempt is made in order to understand the interactions between the protein and the aqueous environment provided by these aggregates.

Fluorescence spectroscopy provides information concerning the degree of polarity in a certain region of the protein, distances between groups and the protein flexibility. α-*Chym* fluorescence arises from eight residues of Tryptophan (Trp) which are very sensitive to distinct environmental parameters, such as temperature, pH, viscosity and ionic strength. This work will also involve the study of N-acetyltryptophan (NAT) since the side chain groups, especially the NH_3^+ group, seem to play a key role in the nonradiative processes.

Bimolecular quenching reactions of these probes agree quite well with the emission spectral data and enabled the evaluation of three different populations of Trp residues in α-Chym. Charged (I^-) and neutral quenchers (acrylamide and succinimide) were chosen to cover the influence of both electrostatic and hydrophobic interactions with nearby groups. The ensemble of the data points to different locations of the probes studied within these reverse micelles as Fig. 1 attempts to illustrate.

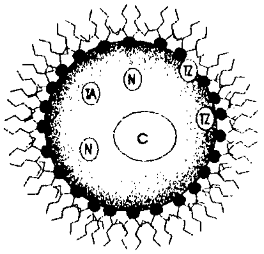

Fig.1- Representative scheme of the predicted locations of Trp, at "pH_{ext}"=7 (TZ) and "pH_{ext}"=10 (TA), NAT (N) and α-Chym (C) in reverse micelles of AOT/*iso*-octane/water at ω_o=20.

RAMAN AND SURFACE-ENHANCED RAMAN SPECTROSCOPY OF TEMPYO SPIN LABELED OVALBUMIN

P11.13

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The biophysical activity of ovalbumin (glycoprotein of 385 amino acids) and its effect in reacting with other enzymes provides contradicting results to the hypothesis of the experiment. Ovalbumin is a good model for the serpin family and a unique feature is that upon proteolysis with enzymes, very little conformational change or inhibitory functions can be observed [1,2]. Raman spectroscopy with its derivative techniques is largely applied in studying the nature of the events produced on biological samples. In particular, due to its high sensitivity and selectivity, surface-enhanced Raman techniques can be successfully used to investigate the conformational changes of proteins, which occur as a consequence of proteolysis, lyophilization or dehydration [3]. A typical stable nitroxyl free radical, widely used as ESR spin label, tempyo (2,2,5,5-tetramethyl-3pyrrolin-1-yloxy-3carboxamide) was applied to solutions of ovalbumin for labelling the protein at various pH (6.7, 8.1, 9.5 and 11). Labeled ovalbumin-tempyo samples were lyophilized and considered for Raman and SERS spectroscopy. Spectra were obtained within the range of 500-1800 cm-1. Several vibrational modes in this region are sensitive to protein conformation, e.g. amide I, amide III and disulfide bond. Raman and SERS spectroscopy is a powerful tool to study binding sites and binding mechanisms of tempyo in the tempyo-protein complex. The spectra of pure ovalbumin at different pHs were compared with the corresponding spectra of the various ovalbumin-tempyo complexes. Pure tempyo sample exhibited intense Raman scattering whereas in the tempyo-ovalbumin complexes the overall contributions of tempyo to the Raman signal were weak. The adsorption of labeled ovalbumin and its orientation on the silver surface is discussed.

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P11.14

TEMPYO LABELED CYTOCHROME C STUDIED BY RESONANCE RAMAN AND SURFACE ENHANCED RESONANCE RAMAN SPECTROSCOPY

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The structure and electronic transfer properties of cytochrome C adsorbed on silver electrodes have been studied by surface enhanced resonance Raman spectroscopy (SERRS) [1]. It was shown that the protein envelope prevents the heme group from coming in direct contact with the metal surface. Cytochrome C on the metal surface may thus be used to study the electron donor and acceptor functions of its heme group. A charge transfer between the cytochrome C and the Ag colloidal surface could elucidate the electron transfer reactions of adsorbed species and provides complementary information in addition to ESR, H-NMR, and IR data. The structure of cytochrome C is very similar to hemoglobin and consists of four heme groups, the active site of this protein. The heme group is a porfirine ring chelate at the Fe(+2) or Fe(+3) and surrounded by a polipeptide chain of 104 aminoacids. The N atom from histidine and S atom from methionine is coordinated at the fifth and the sixth coordinative position of iron respectively. Cytochrome C heme is different from heme group of hemoglobin through the nature of the substituents in positions 2 and 4 (2 thioetheric bounds) [5]. The aim of this study is to elucidate the possible conformational changes of cytochrome C structure with the pH of surrounding medium.

Therefore, Resonance Raman and surface enhanced resonance Raman spectra of tempyo labeled cytochrome C at four pH values (6.7, 8.1, 9.5 and 11) were recorded and analysed in the present work.

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EPR INVESTIGATIONS OF NON COVALENT SPIN LABELLED CYTOCHROME C

P11.15

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Nitroxyl radicals exhibit a number of chemical and physical properties that make them extremely useful molecules for studying biochemical systems, especially the metalloporphyrins. The EPR spectrum can be affected by the motional constrains and orientation of the spin label in the system, by the polarity of the system and by the presence of other species in the system such as reducing agent and paramagnetic ions. Conversely, a spin label can affect the properties of system [1].

The aim of this work was to investigate the Tempyo spin label as a report group for the interactions and the conformational changes of Cytochrome c, as function of pH. Solutions containing cytochrome c and Tempyo nitroxide radical (3-carbamoyl-2,2,5,5-tetramethyl-3-pyrolin-1-yloxy), molecular ratio 1:1 were prepared in phosphate buffer at different pH values (in the range 6.7 – 11) and subsequently lyophilized. The X-band EPR spectra of the solid samples were recorded at room temperature and analyzed by using a program that is available to the public through the Internet (http://alfred.niehs.nih/LMB) for obtaining the magnetic characteristic parameters. The spectra are typical for immobilized nitroxid species, excepting the samples prepared in the acidic pH range, were the paramagnetism is lost. The spectra are similar with those of other noncovalently spin label porphyrins in frozen solution at very low temperatures [2]. Similar spectra were recorded in other nocovalent spin labeled hemic proteins, but in case of nonhemic proteins, the EPR spectra are better resolved. This behavior indicated a possible spin-spin interaction between the hemic iron and the nitroxide group. The small changes in the EPR parameters as function of the pH are discussed in terms of conformational changes of the proteins.

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P11.16

RAMAN SPECTROSCOPY STUDY OF THE INFLUENCE OF P-GLYCOPROTEIN ON THE LIPID MEMBRANE STRUCTURE OF THE MULTIDRUG RESISTANCE CELLS

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Human P-glycoprotein (Pgp), a plasma membrane protein that confers multidrug resistance (MDR), functions as an ATP-dependent drug efflux pump. Since its discovery 30 years ago [1], its molecular mechanism of activity as well as molecular determinants setting drug binding and transport remain to be identified.

Here we present the first Raman spectroscopy study of Pgp within the plasma membrane. We used highly-resistant MDR CEM cancer cell lines, which overproduced Pgp in quantities up to 35% of the total amount of membrane proteins [2]. Raman spectra of the membrane fraction of these cells were compared with the spectra of membranes of the parental sensitive cells presenting exactly the same composition and quantity of each membrane protein except Pgp.

Two sets of spectral lines are presented in Raman spectra of sensitive cell membranes and membranes with overexpressed Pgp. First one corresponds to the lipids: C-C stretch (1000-1130 cm^{-1}); CH$_2$ twist (1297 cm^{-1}); CH$_2$ bend (1440-1450 cm^{-1}); and C=C stretching (1547-1655 cm^{-1}). Second set contains two strong lines 1153 and 1555 cm^{-1} that are attributed to conjugated double bond system.

The high frequency region of Raman spectra contains three main lines at 2850, 2890 and 2930 cm^{-1}. The first two lines are attributed to CH$_2$ symmetric and asymmetric stretching vibrations respectively. The latter one contains vibrational components from Fermi resonance, involving the vibrations of the methylene chain moieties and C-H symmetric stretching modes of the methyl termini of the lipids.

The regions 1000-1130 and 2800-3000 cm^{-1} are very informative in respect to intra- and inter- lipid chain interactions. In particular, relative intensity of peaks at 1090 and 1130 cm^{-1}, assigned to gauche- and trans-conformers, respectively, provide direct measures of intrachain disorder. The 2800-3000 cm^{-1} region can be used to monitor essentially the overall disorder of the lipid acyl chain matrix, but is also sensitive to the intermolecular vibrational coupling and the lateral packing of the acyl chains. Based on our spectral data we conclude that characteristic feature of the Pgp-rich membranes is the increasing contents of gauche conformers of lipid chains.

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RAMAN STUDY OF THE TRIPLEX-LIKE COMPLEX FORMATION OF POLYURIDYLIC ACID AND DIADENOSINE MONOPHOSPHATE : INFLUENCE OF NICKEL IONS

P11.17

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The presence of inorganic ions remarkably influences the nucleic acid structure and stability. Cations in the vicinity of the sugar-phosphate backbone compensate the negative charge of the phosphate groups and therefore stabilize the nucleic acid (NA) conformation. This strongly depends on the cation type; for instance the stabilization efficacy of divalent cations is 100-1000 times higher than that of monovalent ones. Some metal ions can also interact with nucleobases and thus reduce the stability of the NA structure. This is the case of divalent transition metals that are known to create with purine mononucleotides relatively stable macrochelate complexes, where the metal ion is coordinated with both the purine and the phosphate oxygen [1]. Ni^{2+} is known as one of the strongly bound metal ions to NA. In extreme case of very high Ni^{2+} concentration (~ 95mM) even the B-DNA → Z-DNA conformational transition of poly[d(A-T)] is induced [2, 3].

Diadenosine 3'-5' monophosphate (ApA) is known to form preferentially triplex-like complexes with polyuridylic acid (polyU). It has been shown [4] that these complexes can be monitored in aqueous solution by means of Raman spectroscopy. This can be employed to test novel-type modifications of internucleotide linkages for oligonucleotides to be used as new 'antisense' drugs [5]. From this point of view, it is worth knowing how various metal ions can interact with ApA:polyU complexes and thus influence their physico-chemical properties.

In the present contribution the formation, structure and stability of ApA:polyU complexes in the presence of Ni^{2+} have been studied by means of Raman spectroscopy, in monitoring both their concentration and temperature dependencies. The effect of nickel ions is discussed and compared with that of magnesium ions under the same conditions.

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P11.18

FT-IR STUDY OF COMPLEXES DNA-LIPOSOME-METAL ION

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Studies in glassy[1] and gel-solution state[2,3] on complexes of polynucleotides and liposomes with metal ions by means of a variety of techniques, have been reported. The results in part are able to clear the ability of the cation to crosslink the phosphate groups and to modify the C=O modes of polynucleotides base pair and of liposomes bilayers. The influence of each specific fragment of the polynucleotide on the profile of the spectrum of the complex, has been reported[4]. In addition an FT-IR analysis on binary complexes of DNA with some metal cations elucidated DNA conformational and compactisation changes[2]. The purpose of the work was to add further insight in this field and to clear the experimental limits that are mainly due to the limited solubility of the components of the triple complex. Transmittance, DRIFT and CIR spectra have been performed on aqueous solutions of bivalent ions (Ca^{+2}, Mg^{+2}, Mn^{+2}, Co^{+2}, Cu^{+2}), calf thymus DNA, dimyristoylphosphatidylcholine. To obtain satisfactory transparent solutions of the components, a particular mixing procedure has been adopted. Careful deconvolution, second derivative as well as curve fitting treatments have been needed due to overlap of DNA and liposome bands in the spectral regions of interest. The analysis of carbonyl groups of DNA base pairs and of liposomes as well as of phosphate vibrational modes evidenced the formation of the triple complex with spectral features depending on the molar ratio between the components and from the nature of the metal ion. Calcium and Magnesium, Manganese and Cobalt, Copper ions appeared to follow three different interactive patterns. Further knowledge on conformational changes came from the analysis of the C-H stretching region. The analysis of the inter-conversion between A, B and Z forms of DNA on forming the complex in the region 1000-750 cm^{-1}, is already reported. The results have been compared with data from Small Angle X-ray Scattering analysis[5].

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SPECTROSCOPIC CHARACTERIZATION OF CYCLIC GMP IN THE SOLID STATE AND IN SOLUTON

P11.19

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A molecular structure-biological function relationship must exist for cyclic nucleotides, like cGMP and cAMP which underlie important biochemical events .

The aim of this paper is the structural characterization, by Raman vibrational spectroscopy and multinuclear magnetic resonance, of 3'-5'-cyclic guanosine monophosphate, free acid (cGMPH) in comparison with its sodium salt (cGMPNa) both in the solid state and in solution, as an introduction to the study of the molecular interaction of cGMP with biological molecules like, for example, proteinkinase enzyme.

The Raman spectrum of solid cGMPNa shows a strong band typical of the deprotonated N7 guanine residue; on the contrary the solid cGMPH shows a strong band due to the N7 protonated, while both the spectra show the same bands of the PO_2^- group. The same results are obtained with ^{13}C NMR measurements.

An intermolecular OHN7 hydrogen bond and the acidity difference of the two groups (pKa =1 for PO_2H (from diesteric data) and pKa=2.3 for $^{+}N7H$) justify the proton transfer.

A previous x-ray study shows this dipolar form in cGMPH (1) .

The Raman, ^{13}C and ^{31}P NMR solution spectra show an equilibrium between the protonated and deprotonated forms according to the pH value.

The particular dipolar structure of solid cGMPH and its behaviour in aqueous and acid solutions may constitute the structural basis of the cyclic nucleotide biological role.

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P11.20

RAMAN SPECTROSCOPY STUDY OF TOPOTECAN COMPLEXES WITH DNA AND NUCLEOSIDES

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The clinical camptothecin (CPT) derivative topotecan (TPT, hycamtin, NSC609699) is a potent anticancer drug which realizes its activity through the stabilization of the DNA-topoisomerase I (topI) cleavable complex [1]. For many years, the CPTs were described as a unique antitumor compounds exhibiting no chemical reactivity towards DNA alone or the topI alone. In 1998 the mixed observations of the possible interaction between CPTs with the DNA have been reported [2,3]. This work presents the first structural data on the TPT interaction with the calf thymus (CT) DNA without topI as well as with the nucleosides in solution.

Raman spectroscopy reveals direct interactions between the molecular moieties of the E- and D-rings of TPT and dG and dI nucleosides. It should be noted that no any interactions of the quinoline part of the TPT chromophore (rings A and B) were detected within its TPT-nucleoside complexes. This conclusion is based on analysis of the positions and relative intensities of the line at ca. 1620 cm^{-1} assigned to the stretching vibration of the quinoline rings and in the 1563 cm^{-1}÷1426 cm^{-1} spectral region being attributed to the D- and E-rings vibrations. The pronounced differences of the TPT-dG and TPT-dI interactions have been identified. The line at 1309 cm^{-1} downshifts when the TPT is bound to dG, whereas does not for the TPT-dI complexes. Thus, we can infer that the D-E rings of TPT interact with dG via the guanine amino-group.

The Raman spectra of TPT-DNA complexes demonstrate the clear variations of the TPT lines assigned to the D- and E-rings of the chromophores, whereas the lines corresponding to the vibrations of the quinoline part of TPT remain to be unchanged. The most remarkable spectral variations induced by the TPT-DNA binding involve the downshift of Raman lines at 1563 and 1309 cm^{-1}. These lines were shown to be sensitive to the microenvironment of the D- and E-rings of TPT. While the other sensitive to interactions of D-ring lines do not change their positions, it should be supposed, that TPT-DNA binding is determined by the E-ring interactions with the amino-group of dG. The E-ring carbonyl group is the probable candidate for participation in TPT-DNA H-bonding.

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IR-SPECTROSCOPIC STUDY OF EFFECT OF Na^+ ION CONCENTRATION IN SOLUTIONS ON Cu^{2+}-INDUCED DNA STRUCTURAL TRANSITIONS

P11.21

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In our previous works we have shown that on the DNA interaction with Cu^{2+} ions in aqueous solution at ~ 30°C DNA may transit into the compact state, this transition is of positive cooperativity character. In the present work using IR spectroscopy DNA structural transitions under the Cu^{2+} ions action in solutions with different contents of Na^+ ions (0.05÷1 M) were studied.

It was shown that in all the solutions studied the Cu^{2+} ions interaction with DNA leads to the macromolecule transition into the compact state. In the work the dependencies of binding constants and cooperativity parameters ω on the Na^+ content in solution were obtained. It was shown that, when increasing the Na^+ ions concentration in solution, the cooperativity of Cu^{2+}-induced DNA compactisation sharply decreases; the ω dependence on Na^+ ions concentration in solution is of cooperative character. Possible reasons of such a character are discussed.

Also, in the work the results obtained are compared with literature data concerning the effect of Na^+ concentrations in solution on DNA compactisation and aggregation. It was shown that, regardless of the compactisation agent valence, cooperativity of the DNA compactisation process decreases with the increase of the Na^+ ion concentration in solution. Besides, the more the condensation agent valence the higher cooperativity of the compactisation process.

The decrease of the cooperativity of the DNA compactisation process with the rise of the Na^+ ion concentration in solution is explained by the competition between Cu^{2+} and Na^+ ions for binding sites on DNA phosphate groups as binding constants of Cu^{2+} ions are strongly dependent on the concentration of monovalent ions in solution and decrease with the concentration rise.

P11.22

STUDY OF STRUCTURE AND STABILITY OF Ni^{2+} COMPLEXES WITH POLYA×POLYU AND POLYA×2POLYU.

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Ni^{2+} ion interaction with polyA×polyU (A×U) and polyA×2polyU (A×2U) in buffer solutions (pH 6, 10^{-2}, 3×10^{-2} M Na^+) was studied by the methods of differential UV spectroscopy and thermal denaturation.

At 20^{0}C A×U and A×2U have some number of disordered links. Addition of Ni^{2+} restores the polymer helical state. Coil→helix transition is coursed by Ni^{2+} binding to oxygen atoms of phosphate groups of disordered one-stranded polyA regions. Up to 0.03M Ni^{2+} ions do not interact with adenine and uracil heteroatoms of A×U and A×2U.

Diagrams of phase equilibrium between one-, two- and three-stranded polynucleotide conformations in dependence on temperature and Ni^{2+} content have been obtained. Ni^{2+} ions increase A×U and A×2U thermostability in the whole range of Ni^{2+} content. Melting interval and the cooperativity parameter concentrational dependencies have extreme. Ni^{2+} ions induced increase of A×U and A×2U melting temperatures is mainly due to the differences in Ni^{2+} binding to multyhelical structures and polyU.

Obtained data on A×U and A×2U thermostability permit us to calculate association constants of Ni^{2+} binding to A×U and A×2U within the framework of equilibrium binding theory [1]. Ni^{2+} interaction with the polynucliotides is characterized by the negative cooperativity. This result is in the qualitative agreement with the data on Mg^{2+} binding constants [2]. At 3×10^{-2} M Na^+ Ni^{2+} association constants corresponding to zero binding degree are 8×10^4 M^{-1} and $6\times10^4 M^{-1}$ for A×U and A×2U respectively. The correlation of Ni^{2+} binding constants values and linear charge density on polynucleotides surfaces is observed.

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INCREASE OF IR ABSORPTION BANDS INTENSITY AT DNA TRANSITION INTO COMPACT STATE

P11.23

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In our recent work[1] we have shown that intensity of absorption bands of DNA phosphate groups and bases is increased at DNA interaction with divalent metal ions in aqueous solution. We explained the increase observed by DNA compactisation at metal ions binding (it is known that IR band intensity may be increased at polymer transition into high-ordered state). To verify whether DNA compactisation may results in such strong (3-4 times in case of DNA interaction with Cu^{2+} ions) increase of absorption band intensities in the present work we studied IR spectra of DNA complexes with Tb^{3+} ions (Tb^{3+}, among with other 3^+-ions, induces DNA compactisation in solution).

IR spectra of DNA complexes with Tb^{3+} and Cu^{2+} ions show that binding of both Tb^{3+} and Cu^{2+} ions to DNA leads to the sharp increase of band intensities; the character of the intensities increase is similar for these ions. Comparing Tb^{3+} concentrations at which the intensity increase occurs with ones at which DNA compactisation in solution took place[2] we conclude that intensity of absorption bands at DNA transition into compact state is increased.

Dependencies of relative intensity increase on total metal concentration are shown in fig.1. One can see the character of all dependencies (sharp increase of bands intensity in narrow interval of metal ion concentration) is similar. Thus we can conclude that bands intensity increase shown in [1] may occur at DNA transition into compact state. Metal ions activity in this process correlate with their affinity to DNA phosphate groups. At high Tb^{3+} ion concentration DNA condensation is replaced by its partial denaturation and precipitation.

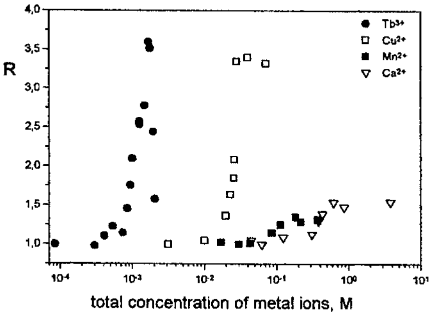

Fig.1. Dependencies of relative intensity R ($R=D_i/D_0$, where D_0 - the optical density of the absorption band of DNA without divalent metal ions, D_i - the optical density of the absorption band of DNA complex with the i-th metal ion concentration) on total metal ion concentration for absorption band at ν=1090 cm^{-1} for DNA complexes with three- (Tb) and divalent (Cu, Mn, Ca) metal ions.

On the basis of the results obtained it is possible to estimate the binding constants of metal ions with DNA and cooperativity parameter of DNA compactisation process. We also proposed the model of DNA intra- and intermolecular condensation at divalent metal ions binding (the latest is very important to take into consideration as we used a concentrated DNA solution).

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P11.24

INTERACTION OF DNA WITH AN AMINOOXY ANALOGUE OF SPERMIDINE. AN FT-IR AND FT-RAMAN APPROACH

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Biogenic polyamines are essential molecules for all living organisms, from microorganisms to superior plants and animals [1]. In the last twenty years, experimental evidences about direct interaction between polyamines and DNA have been achieved. Nevertheless, the problem of how they link remains unresolved. Among the different ways to thoroughly understand the molecular physiology of natural polyamines, the study of structural analogues has demonstrated to be a powerful tool.

Because many of the biological functions of polyamines can be attributed to their polycationic properties at physiological pH, a series of aminooxy derivatives have been recently synthesized to study the role of charge distributions and structural requeriments in the molecular physiology of natural polyamines [2]. 1-aminooxy-3-N-(3-aminopropyl)-aminopropane, AP-APA, is an aminooxy analogue of spermidine in which one $-CH_2-NH_3^+$ group has been substituted by the $-O-NH_2$ group, Figure 1.

$NH_3^+-CH_2-CH_2-CH_2-NH_2^+-CH_2-CH_2-CH_2-CH_2-NH_3^+$ spermidine

$NH_3^+-CH_2-CH_2-CH_2-NH_2^+-CH_2-CH_2-CH_2-O-NH_2$ AP-APA

Figure 1. Chemical structures of the biogenic polyamine spermidine and its aminooxy analogue.

Because the pK_a of an amino terminal group is significantly lower than the pK_a of the aminooxy group, this molecule is partially deprotonated at physiological pH. We therefore have an analogue with similar size and shape than spermidine, but with lower charge at physiological pH.

In a previous paper [3] the interaction between DNA and the ornithine-derived polyamines (spermine, spermidine and putrescine) has been investigated by Raman spectroscopy. In the present work we paid attention in analysing by vibrational spectroscopy the structural specificities of the AP-APA/DNA interaction. FT-IR and FT-Raman spectra of solutions containing highly-polymerized calf-thymus DNA and AP-APA, at different molar ratios, were recorded. Both natural and heavy water were used as solvent. Spectral changes were interpreted in terms of preferential sites of binding in the aminooxy/DNA complexation, making correlations with spermidine molecule.

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SPLITTING OF INFRARED BANDS OF MONONUCLEOTIDES IN AQUEOUS SOLUTION

P11.25

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This article presents an study based in analysis of infrared spectra in aqueous solution of natural mononucleotides 5'-GMP, 5'-CMP, 5'-dAMP, 5'-TMP, and their analogues showing antitumoral activity 5'-araCMP and 5'-araAMP.

Some of the IR bands in the spectra of these compounds in ^2H_2O solution and pH 7-8 split clearly into at least two components at medium-high concentration, as it is revealed by the second derivative or, in some cases (particularly at high concentrations), by direct inspection of the bands. The signals showing this behaviour are mainly those assigned to the phosphate group (in all the analysed systems)[1,2,3] and several bands due to normal modes with high contribution of base stretch motions. That is the case of the 1625 cm^{-1} IR band in 5'-dAMP and 5'-araAMP[4], the 1690, 1660 and 1628 cm^{-1} bands in 5'-TMP, the 1504 and 1524 cm^{-1} bands in 5'-CMP and 5'-araCMP and the carbonyl stretching bands (1665-1645 cm^{-1}) in 5'-CMP, 5'-araCMP, and 5'-GMP[1,3]. The splitting increases with concentration; it is fairly symmetric and it is accompanied by an important increase of band width.

The high contributions of groups or molecular fragments with significant dipolar moments to the normal modes giving rise to these bands allow us to ascribe this effect to dipolar coupling processes or interactions with the solvent.

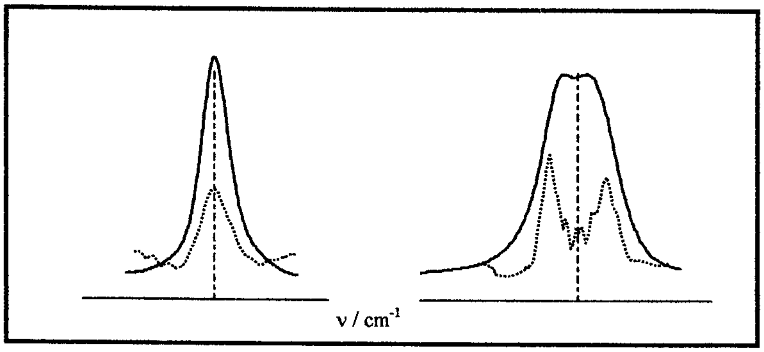

Figure 1. Experimental profile and second derivatives with sign changed (dotted lines) of the FTIR band at 1625 cm^{-1} of 5'-dAMP in ^2H_2O solutions at low (left) and high concentration.

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P11.26

FTIR SPECTROSCOPY STUDIES OF TUMOUR NUCLEIC ACIDS

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Last years in the genetic investigations, spectroscopic methods-along with traditional methods- are widely used for nucleic acid analysis. A modification of DNA molecules isolated from cancer and other type of modificated tissues is a subject of great interest. Drastic differences in FTIR spectra of DNA from breast cancer tissues and normal one have been already revealed [1]. A creation of new forms of DNA under the exposition to environmental chemicals, have been concluded by the same authors [2]. Earlier we have applied vibration spectroscopy for diagnostics of brain tumor at different stages of malignancy and have obtained some results [3].

In this paper we present FTIR-spectroscopy data for RNA (total fraction) and genomic DNA, isolated from the brain tumor tissues of experimental animals. The Bruker IFS-48 instrument for registration spectra and Opus 2.2 program for decomposition of complex bands have been used.

We have registered changes in DNA and RNA isolated from tumor cells in the 3 spectral regions -3500-2700 cm-1, 1800-1400 cm-1 and 1400-800 cm-1. The most prominent changes have been observed in the vibrations of phosphate groups in the 1300-800 cm-1 region and in the region of the stretching vibrations of OH, NH and CH groups. The changes in the tumor DNA and RNA in phosphate bands seems to be caused by some conformational changes which involve the positions of phosphate groups in DNA and especially RNA helix and breaking of old H-bonds between the bases which can be accompanied with the formation of new H-bonds. A great amount of statistical data, creation of a library on FTIR data of native nucleic acids from different types of normal and tumour tissues, as weel as good mathematical approaches are needed for the usage of these data as diagnostic criteria.

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BANDS SPLITTING IN THE IR SPECTRA OF SOME 5'-GMP AND 5'-CMP DERIVATIVES RELATED TO ORDERED ARRANGEMENT OF THESE NUCLEOTIDES

P11.27

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The IR spectra of some 5'-GMP and 5'-CMP derivatives in solid state show splitting of bands related to group with strong dipolar moment, such as carbonyl and phosphate groups. This effect can be related to the dipolar coupling of two or more groups due to their nearness and set position in these derivatives [1-4]. This is also supported by the ^{13}C NMR CP-MAS spectra of solid samples. The distance between these groups in the sample can be estimated from the equation that relates magnitude and relative position of the dipoles with the splitting produced in the vibrational spectrum [3]. The relative position between nucleotides in natural polynucleotides, such as DNA or RNA, should give rise to similar effects in their IR spectra. Therefore, these results should be taken into account when it comes to interpret the spectra of this macromolecules.

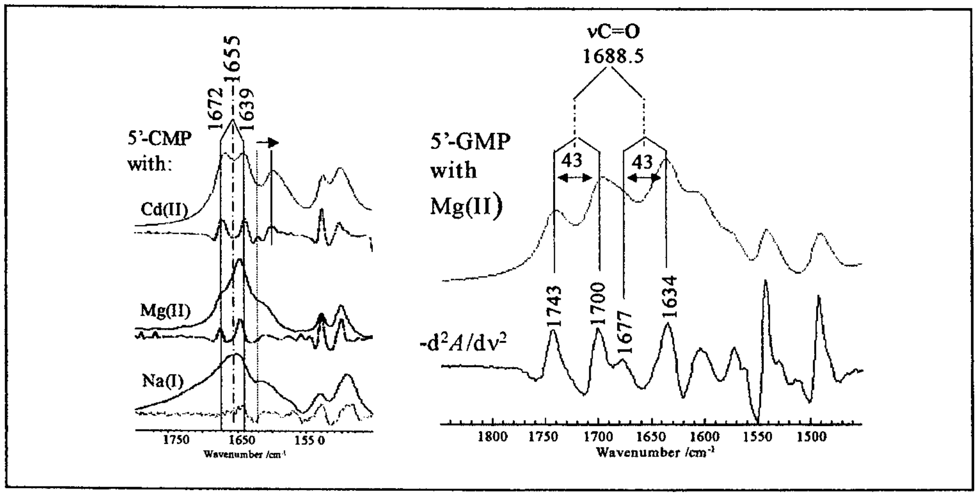

Fig 1. Vibrational spectra (1800-1500 cm^{-1}) in solid state and second derivative with sign change of the IR spectra ($-d^2A/d\nu^2$).of the disodium salt of 5'-CMP and their complexes with Mg(II) and Cd(II), and of 5'-GMP with Mg(II).

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P11.28

FT-IR STUDY OF ANOMERIC PENT-2-ENOPYRANOSIDES

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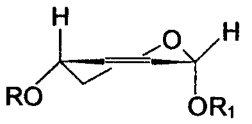
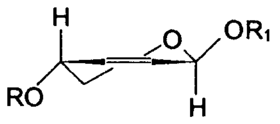
Alkyl dideoxyhex-2-en-erytropyranosides constitute useful substrates for a synthetic approach to antibiotic ristomycin components[1]. In an NMR study on ethyl-α- and β-D-*glycero*-pent-2-enopyranosides, it has been suggested that each of these compounds can exist conformationally pure in half chair form having a proper anomeric effect. Hydrogen bonding between the OH group and the ring oxygen did not appear to play an essential role to justify the inertness of the β- anomer to undergo oxidation by means of manganese dioxide, although NMR were not able to clarify this behaviour[2]. Recently, the role of FT-IR technique has been evidenced as a complementary tool in structural studies of diasteromeric forms[3]. In this work we used infrared spectroscopy to investigate conformational differences in alkyl α- and β-D-*glycero*-pent-2-enopyranosides (α, β), (1: R = H, R_1 = isopropyl; 2: R = H, R_1 = benzyl) (3: R = OAc, R_1 = isopropyl; 4: R = OAc, R_1 = benzyl) in order to evaluate if intra- and intermolecular hydrogen bonding can be in part responsible of the particular behaviour to oxidation. The analysis of OH and other moieties from spectral data in 1 and 2 in neat, in hexane solution and in $CHCl_3/CCl_4$ mixture evidences differences between the anomers mainly due to solvent effect. Support to BatchMin V.5.5 simulation that showing that anomers α are less stable anomers than β, comes from the inspection of the free and bonded OH modes. The frequency and the energy of $\nu_{C=O}$ stretching modes in derivatives 3 and 4, confirms that influence of steric hindrance and intramolecular bonding are rather different in these anomers. The band at *c.a.* 885 cm^{-1}, present only in anomers α, that can be tentatively attributed to the γC(2)-H mode, resulted of diagnostic importance in the assignment of the conformation.

α



β



R = -H, -COMe
R_1 = isopropyl, benzyl

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FOURIER TRANSFORM INFRARED STUDIES OF MELITTIN, VITAMIN D_3 AND DIPALMITOYLPHOSPHATIDYLCHOLINE

P11.29

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The perturbation induced by melittin (9 mole %) and vitamin D_3 (3 mole % or 12 mole %) on the molecular organization of dipalmitoyl phosphatidylcholine (DPPC) in the form of dry liposomes and in D_2O solution were studied by using FTIR spectroscopy. The amide II / amide I (A_{II}/A_I) peak-height intensity ratio is known to be sensitive to structural changes involving the aggregation properties of the polypeptide and gives a rough idea of the existence of tetrameric or monomeric units of melittin in the system. Lower values of this ratios which is found between 0.52-0.45 demonstrate that melittin exists as a monomeric form in the binary mixture of melittin-DPPC and ternary mixture of DPPC-vitaminD_3-melittin. The addition of melittin and vitamin D_3 in DPPC causes only a slight increase in the intensity of the 1090cm^{-1} band. This band is associated with the C-C stretching mode of gauche conformers. The intensity of the 1090 cm^{-1} band relative to that of the 1060 cm^{-1} band which is assigned to the C-C stretching vibration of chain segment in the trans conformation, increases in the presence of melittin. With the addition of 12 mole % Vitamin D_3 into the melittin-DPPC system, induces only a slight increase in this ratio, illustrating decrease in the conformational order. Whereas addition of 3 mole % vitamin D_3 into the same system causes opposite effect. Solution studies of this system in D_2O give completely reverse effect in comparison to dry state. In dry state the out-of phase CH_2 scissoring frequency value of fully extended acyl chains at 1468 cm^{-1} is not affected by the presence of melittin and vitamin D_3. On the other hand, a slight increase is observed in the intensity of this band. The interesting changes were also observed in the C=O stretching band of the melittin-vitamin D_3 containing DPPC mixture in comparison with pure DPPC. An increase and a decrease were observed in the intensity of the carbonyl-stretching mode in DPPC in the presence of melittin-3 mole % vitamin D_3 and melittin-12 mole % vitamin D_3, respectively. The rearrangement of the bilayers also affects the head group moiety: The asymmetric phosphate vibrational band shifts to lower frequencies with the addition of melittin in the presence and absence of vitamin D_3. The relative intensity of this band is increased in both dry state and D_2O.

P11.30

THERMODYNAMICS STUDY OF VITAMIN D_2-GRAMICIDIN S-DIPALMITOYLPHOSPHATIDYLCHOLINE MODEL MEMBRANE INTERACTIONS BASED ON FTIR SPECTROSCOPY

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The Fourier transform infrared spectroscopy was used in this study to investigate the reversibility and thermodynamics of the main-phase transition of DPPC model membrane alone and in the vicinity of the antibiotic peptide gramicidin S (GS). Investigation of the reversibility was performed by a continuous extension of our experiments carried out as temperature is cycled gradually. In phosphate buffer of pH 7.4, the main phase transition behavior of DPPC and the effect of gramicidin as a function of temperature over the temperature range 25-60 °C were observed to be reversible upon temperature recycling. Based on these observations of reversibility and on the two-state transition of DPPC, the linear extrapolation method was employed to monitor the stability of GS-DPPC interacting systems at different peptide concentrations. This approach has been previously applied on melittin-membrane interactions.[1]. The presence of GS has been observed to induce a direct perturbation in the packing of acyl chains as concluded from the decrease in T_m and ΔH_m as GS concentrations are raised. This result agrees with the previous calorimetric studies that reported a decrease both in ΔH_m and T_m [2,3]. Furthermore, an evident reduction in the maximum stability energy ΔG_s of DPPC was also observed with increasing incorporation of GS amounts. This indicated a destabilization effect imposed on the acyl chains of DPPC by GS presence, which results from the strong interaction of this peptide with DPPC model membrane. The effect of different vitamin D_2 concentration on gramicidin S - membrane stability and phase transition has been also investigated by thermodynamic method based on FTIR results. Further measurements of entropy change ΔS_m were carried out to yield insights regarding the dynamics of the different investigated systems. These estimates observed by employing the thermodynamics approach are shown to be in good agreement with the FT-IR spectral estimates.

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THE EFFECT OF SELENIUM - VITAMIN E DEFICIENCY AND SELENIUM EXCESS ON BONE MINERAL AND AMIDE MATRIX, MEASURED BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

P11.31

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The present study investigates the effect of selenium and vitamin E on rat bone by Fourier transform infrared spectroscopy, especially on the mineral and protein matrix. For this purpose the newborn rats of both sexes were fed with either a control, or selenium and vitamin E deficient or selenium excess-vitamin E adequate diet. The FTIR spectrum of calcified tissue provides information on the structure and environment of carbonate and phosphate groups of the mineral phase, as well as the organic matrix expressed as Amide I and II. The mineral to matrix ratio calculated from the ratio of integrated areas (phosphate ν_1 and ν_3 bands at 900-1200 cm^{-1} to the amide I band at 1600-1720 cm^{-1}) increases for selenium-and vitamin E deficient or selenium excess-vitamin E adequate diet in comparison to control group. This ratio for femur is found to be less than those of tibia. An increase in the ratio of band areas of the total carbonate (based on ν_2 band at $\approx$ 850-900 cm^{-1}) to the phosphate ν_1, ν_3 bands are also observed. However, the order of increase of this ratio is less than the mineral to matrix ratio. The increase in CO_3^2/ PO_4^3 ratio can be due to higher rate of decrease in PO_4^3 content as CO_3^2 content also decreases. The unstable carbonate content is decreased as in the case of type A (CO_3^2 ions substituting for OH^-). In the present study Lipid/protein ratio were also calculated. This ratio is found to be decrease as the mineral to matrix ratio increases. The changes in the frequency and the relative intensity of the bands observed in the region of 3000-2800 cm^{-1}, which mainly contain contribution from lipids, are related to the diet. For this reason, both qualitative and quantitative diet induced changes in bone are observed. The interesting result is that the excess and deficient diet show the same type of effect on bone lipid, mineral and protein matrix which is in agreement with our earlier biomechanical and crystallinity results [1]. The results obtained implicate that the bones are one of the major target organs in intoxication as well as deficiency syndrome.

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Biospectroscopy (2)

-Bio-systems and organs

DYNAMIC AND EVOLUTIONARY ASPECTS OF CHIRAL SYMMETRY BREAKING PHENOMENA IN PROTEINS AND LIVING ORGANISMS

P12.1

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Chiral symmetry breaking phenomena in living organisms have been discussed intensively for years using many interesting interdisciplinary ideas [e.g. 1]. Some of them base on stereochemical properties of biomolecules, some indicate that homochirality is a result of processes that occur at different levels of complexity of chemical systems. It is suggested that energetic differences between two enentiomeric forms occur when fundamental symmetries are broken [e.g. 2] This effect, which is extremely weak, can be preserved and amplified at the chemical level using various chemical processes like molecular decay [3] or aurokatalytic reactions [e.g. 4]. An interesting point of view was presented in [5]. The author discusses the role of external collinear electric and magnetic fields in producing chiral products of unimolecular reactions of achiral molecules. Since external conditions (like gravitational field and, in some cases, electromagnetic fields) are important for biological objects this approach seems to be especially useful for investigations at the biological level.

The presented ideas have inspired me to propose a theoretical model, based on some analogies to the CPT theorem, that applied to living organisms allows me to distinguish between a living organism and its mirror form. The model treats molecules and organisms as complex, dynamic forms existing in external environment. I analyse basic processes like protein biosynthesis or decay that occur in living organisms and could influence or amplify chiral symmetry breaking. Since biological processes depend on protein structures I consider also structural features of natural proteins. The model partially explains discussed previously [6] characteristic features of natural proteins like distribution of amino acids having electric charges in protein helices and left-handed endings of helices. Such features have occured during molecular evolution therefore some evolutionary conclusions can be also made. The model is theoretical, but I hope that its elements could be experimentally tested.

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P12.2

INVESTIGATION OF BIOLOGICAL SYSTEMS USING INFRARED SYNCHROTRON RADIATION AT BESSY II

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In 1997 the IFV (Interdisziplinärer Forschungsverbund) Strukturbiologie Berlin started an initiative with scientific groups working in the fiels of infrared spectroscopic applications and infrared spectroscopic methods: IRIS (Infrared Initiative Synchrotron Radiation). The aim of IRIS is to develop an IR facility at BESSY II (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung) for the near, mid and far infrared wavelength region and to make it accessible to the interested scientific community for a broad field of applications. This beamline will be equipped with an infrared Fourier transform spectrometer, an infrared microscope as well as an ellipsometer for life and material science investigations. The planned scientific activities include structural-biological research by means of Fourier transform spectroscopy and time resolved investigations of biological systems as well as new developments in spectroscopic methods. It is planned to perform investigations on proteins, on biological tissues down to single cells, high-pressure and microsample measurements in the far infrared region and to investigate surfaces and thin films by apllying infrared ellipsometry with a high lateral resolution.

In current work on biological systems we investigate the temperature and pH dependence of the equilibrium of the rhodopsin intermediates Meta I and Meta II and the influence of Gt derived peptides on this equilibrium by infrared spectroscopy. This work was performed by a Bruker ivs 113v FT-IR spectrometer equipped with a conventional globar as light source.

What benefit comes from using synchrotron radiation for this kind of measurements?We plan similar experiments with mutant rhodopsins and retinal analoga which are only available in very samll amounts. The brightness of synchrotron radiation allows an extremely small focus of the beam on the sample. This will decrease the required amount of sample considerably and renders possible IR measurment which could not be done with a conventional light source.

Another topic is the FT-IR investigation of the nature of H^+, Li^+ and Na^+ motins in gramicidin which is used as an antibiotic agent. Understanding the ion translocation via ion channels through gramicidin is of utmost biophysical and midical relevance, because it leads to a deepter insight into the mechanism of ion conduction in membrane proteins in genereal.

We plan to extend this measurements to the K^+ and Cs^+ complexes of gramicidin and related compounds. We exprect the so called continous absorptions, caused by fast motions of K^+ and Cs^+ in the channel, in the range between 100 and 10 cm^{-1}. They should be very broad and of low intensity. Sanchrotron radiation provides an important tool for measurments in the far infrared region because the brightness in this spectral range is about 1000 fold higher than in conventional light sources.

FTIR SPECTROSCOPY OF COMPLEXES FORMED BETWEEN METARHODOPSIN II AND C-TERMINAL PEPTIDES FROM THE G-PROTEIN α- AND γ- SUBUNITS

P12.3

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Absorption of light by rhodopsin leads to retinal isomerization and relaxation into the metarhodopsin intermediates, Meta I and Meta II. Metarhodopsin II provides the active conformation R* for interaction with the heterotrimeric G-protein, Gt. The Meta I/Meta II conversion requires two proton transfer steps, namely deprotonation of the retinal Schiff base bond and proton uptake from solution, with conserved residues Glu^{113} and Glu^{134} as likely proton acceptors. The final product of the sequence of intermediates is protonated Meta II. We enriched this form at low pH and analyzed its FTIR difference spectrum by a global fit procedure. It was then investigated whether C-terminal synthetic peptides (Gtα(340-350) and Gtγ(60-71)farnesyl) can recognize and stabilize metarhodopsin conformations other than protonated Meta II. Both peptides cause virtually identical spectral changes that are not seen with control peptides (Gtα (K341R, L349A) and non-farnesylated Gtγ). The spectra reflect all the protonation dependent bands normally observed when Meta II is formed at acidic pH. We conclude that the interactions of rhodopsin with both the Gtα- and Gtγ peptide require the protonated Meta II species, suggesting that the related receptor sites are inaccessible in all other conformations. Unique microstructural changes in the receptor´s signaling state may allow the access of the Gt C-terminal structures. Beside the protonation dependent bands, additional features, again very similar with both peptides, appear in the amide I and II regions. They may indicate induced fit in the peptides and/ or receptor interaction domains.

P12.4

INVESTIGATION OF SCATTERING SPECTRA AND TRICHROMATIC COORDINATES OF EYE LENS

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Investigation of spectral characteristics of light scattered by eye lens has great diagnostic importance. In this study, we investigated scattering spectra of human intact cataract lens experimentally and theoretically. Dependences of chromatic characteristic versus the scattering angle were presented on chromaticity diagram [1].

We have used pencil beam of 2.5 mm in diameter with wavelength varying from 420 to 680 nm. Measurements were held by two methods: in the first method the light scattered into proximal and distal hemisphere diffuse reflectance was collected separately by integrating spheres. In the second one the limitation of scattered light pinholes gave he possibility to control scattering angle and location of the volume under investigation inside the lens.

Modeling of multiple light scattering by the Monte-Carlo methods were held in the theoretical part of the work. We use suspension of polidisperce spherical particles placed in the volume, bounded by two spherical surfaces as the eye lens model. Scatterers size distributions were calculated by aggregation theory [2]. Scattering of light was described by Mie formulas [3]. We develop the Monte-Carlo method, which accounting the polarization effects of scattering. It gave us possibility to compare chromatic characteristic of polarized and natural light. Angular dependencies scattered light spectra versus particle concentration and order of scattering were obtained.

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INFRARED EMISSION FROM PHOTOEXCITED BACTERIORHODOPSIN: STUDIES BY FOURIER TRANSFORM SPECTROSCOPY.

P12.5

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Bacteriorhodopsin (BR) is the light-transducing protein in the purple membrane of *Halobacterium salinarium.* The retinal is the chromophore, which is attached to the protein through a protonated Schiff base linkage with lysine. This pigment intensively absorbs visible light and practically does not fluoresce. Along with the photochemical transformations of light-excited molecules, only weak fluorescence can be observed in the near-infrared region. In present work, using FT-IR technique we were able to register the infrared emission from BR thin film under continuos illumination by visible light (from100 Xenon lamp) at room temperature. This radiation is not induced by temperature rise, it has a discrete spectrum in infrared range from 400 up to 4000 cm-1, at which one there are bands relating the chromophore. By comparing these results with resonance Raman and FT-IR difference data the majority of stretching vibrations can be identified. The agreement in the frequency of bands assigned to the BR's chromophore is very good whereas the difference occurs in the intensity distribution among characteristic bands as for the parent BR568 state so for the other intermediates of BR 's photocycle. A wavelength of exciting light strongly effect on the IR-emission spectra.

P12.6

TIME-RESOLVED MULTICHANNEL MICROSPECTROFLUORIMETRY

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Lifetime sensitive fluorescent indicators are used to monitor intracellular parameters (membrane potential, local pH, Ca^{2+} and other ions.) [1]. Non specific interactions of the indicators with the cytosolic proteins, substantial contribution of the fluorescence background of endogenous chromophores (e.g. NADH or flavins) or photoinduced dye bounding, influencing the fluorescence signal in the complex intracellular medium can be resolved by means of multiwavelength lifetime measurement.

The UV confocal laser microspectrofluorimeter was adapted for fluorescence lifetime measurements using multifrequency phase modulation technique. The frequency domain method with a modified optical multichannel detector is used as originally described in [2]. The technique is based on a harmonic response of the fluorescence signal. Both excitation laser beam intensity and optical detector gain are high frequency modulated (from 1 to 300 MHz). Resulting fluorescence signal is of the same frequency and its phase and the modulation depth are fluorescence lifetime dependent. Relative phase angle and relative modulation values of the fluorescence signal are determined for each spectral point.

However, complex fluorescence spectra containing several lifetime components are obtained in such a case. Lifetime-based spectral decomposition (by using a minimization procedure) is then inevitable to made single component analysis of the complex intracellular fluorescence spectra.

Spectral contribution of TMRM fluorescence probe with hypericin and hypocrellin-A mixture in DMSO solution was first obtained by this way. Each individual spectral component was characterized by its specific fluorescence lifetime and actually corresponded to the previously published data [1]. Intracellular binding of Snarf1 AM probe (intracellular pH indicator) was successfully studied on single mouse fibroblast (3T3 cell line). Three lifetime components representing protonated free form (0.66 ns), unprotonated free form (1.22 ns) and intracellular bounded form (4.2 ns) were determined in agreement with [3,4]. These results proved that the multiwavelength phase modulation fluorescence spectroscopy is a powerful tool for intracellular lifetime studies.

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AB INITIO AND SEMI-EMPIRICAL CONFORMATIONAL STUDIES OF PYRIDOXAL-5'-PHOSPHATE DERIVATIVES

P12.7

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It is known that pyridoxal-5'-phosphate (PLP), the biologically active coenzymic form of the vitamin B_6 compounds essential for many enzymatic reactions, can also modify proteins and influence their functional states and properties. Carbonyl group of PLP interacts with amino groups to produce reversible complexes (Schiff bases) and stable adducts (secondary amines).

Conformational studies for reversible complexes and stable adducts of PLP with amino acids were performed using Hartree-Fock ab initio (3-21G) and semiempirical (AM1, PM3) calculations. Conformational energy surfaces versus torsional angles for PLP complexes with glycine, L-valine, L-tyrosine, and L-tryptophan were calculated with the use of GAMESS. During the structure optimization these torsional angles were fixed and the other parameters varied.

Two conformational states (another two are symmetrical relative to the ring), differed by carboxyl group orientation with regard to pyridine cycle, were found for stable adducts of PLP with aliphatic amino acids (Fig.2). For complexes of PLP with tyrosine or tryptophane situation is more complicated due to interaction between pyridine and aromatic rings.

On the base of computational studies results, photochemical and time-resolved fluorescence data we suggest a possible scheme of excited states deactivation for PLP-amino acid complexes.

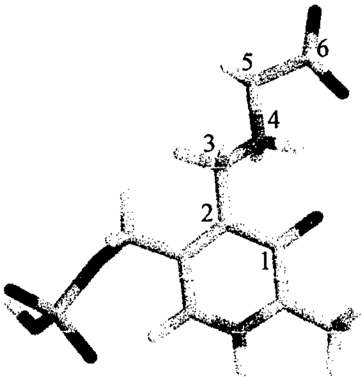

Fig.1. Stable adduct of PLP with glycine.

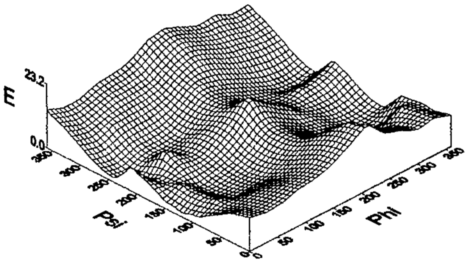

Fig.2. Conformational energy surface versus torsional angles Phi (1234) and Psi (3456) for PLP-glycine stable adduct. Numbers correspond to atoms in Fig.1.

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P12.8

QUANTITATIVE ANALYSIS OF APOPTOTIC CELL DEATH USING INFRARED SPECTROSCOPY

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Apoptosis is a programmed, physiological mode of cell death that plays an important role in the pathogenesis and progression of cancer. Quantitative analysis of apoptosis has become an important issue in patients with acute lymphoblastic leukemia. Since infrared spectroscopy can simultaneously detect changes of cellular DNA and proteins (see refs. 1,2), we hypothesed that IR could determine the percentage of apoptotic leukemia cells. To this end, we treated a T-lymphoblastic cell line with etoposide, an anti-neoplastic agent, to produce apoptosis. The percentage of apoptotic cells after treatment was determined by standard flow cytometry. An analysis of the infrared spectra of these apoptotic cells showed obvious changes in such cellular components as lipid, protein and DNA. As the percentage of apoptosis in these cells increases, the dominant protein of the treated cells shifts from α-sheet to β-helical, the lipid content increases and the amount of detectable DNA decreases. To establish whether the differences between the control and treated cells are statistically significant, we used the entire spectral region instead of the traditional single band analysis. The t-test results show that the spectral differences between the control and apoptotic cells are statistically significant and that these differences are time dependent after the drug treatment. Furthermore, by correlating the overall spectral changes of the treated cells with the percentage of apoptotic cells detected by the reference flow cytometry method, we found a direct temporal relationship between these two methods regarding the severity of apoptosis. In fact, IR spectroscopy showed a higher sensitivity for detecting apoptosis than flow cytometry, suggesting that the former may provide a fast and reagent free means for the quantitation of apoptotic cells in leukemia patients.

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VIBRATIONAL BIOSPECTROSCOPY: WHAT CAN WE SAY ABOUT THE SURFACE WAX LAYER OF NORWAY SPRUCE NEEDLES?

P12.9

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The epicuticular layer on Norway spruce [*Picea abies* (L.) Karst.] needles is an important interface between the tree and air, bringing interesting information about the response of the tree to the conditions of growth and also to the environmental stress. The needles of trees growing in polluted areas, observed under the scanning electron microscope, exhibit different types of injury to epicuticular wax layer as well as changes in chemical composition, documented by chromatographic methods. There are several drawbacks of these methods and so we have studied [1] a potential of the FT Raman spectroscopy to serve as a screening method of these changes.

There are several *a priori* limitations of this application, but as R. Anthony Shaw and Henry H. Mantsch pointed out: *The idea of using vibrational spectroscopy to explore the properties of living organisms is as absurd as it is compelling* [2]. What is the real chance of vibrational spectroscopy to distinguish small chemical changes of two biological objects?

This contribution summarizes our experience with measurement and chemometric evaluation of the FT Raman spectra of the Norway spruce needles by macro- and microscopic techniques, and also infrared spectra by ATR technique [3] on a large sampling set collected in all seasons in the course of years 1997 - 1999 in several places of the same locality and also on the several localities of the Czech Republic.

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P12.10

FTIR SPECTROSCOPY AS A TOOL TO ANALYZE SURFACE OF NORWAY SPRUCE NEEDLES

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The surface of needles is covered by a waxy layer, which protect the underlying cells from various influences of climate and air pollution. Properties of this layer have been frequently studied by scanning electron microscopy (SEM) and by chromatography. Recently, we have reported a study of surface of Norway spruce needles by FT Raman spectroscopy [1]. Now we present the possibilities of FTIR spectroscopy using ATR technique.

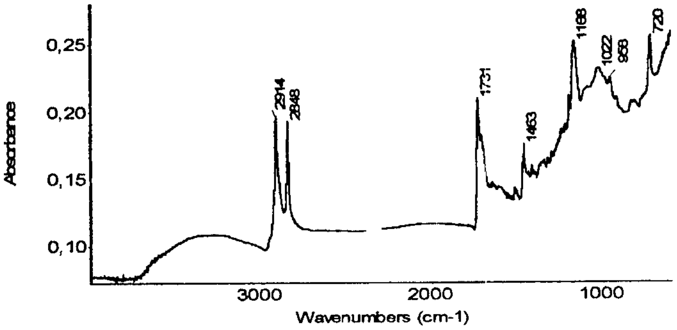

Fig. 1 - ATR spectrum of Norway spruce needle

ATR accessory equipped with ZnSe crystal was used to obtain spectra of needles fixed by micrometer-controlled compression clamp. The spring tension was optimized to prevent injury of needles and to ensure repeatability of spectra (Fig. 1). Then, needles of selected trees of six forest areas of the Czech Republic were investigated. Two methods were performed for chemometric evaluation of ATR spectra. The principal component analysis (PCA) provided a view of data variability, an outliers identification, clustering and models creation. The place on the needle, the position of the twig on the branch, the age of the needle, selected tree of particular forest area and forest area was used as category variable. The classification method SIMCA enabled to compare models created on the basis of PCA showing the importance of the age of needles and dissimilarities of some individual trees.

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P12.11

SPECTROSCOPIC STUDY ON THE *IN VITRO* DEGRADATION OF A BIODEGRADABLE COMPOSITE PERIODONTAL MEMBRANE

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Biodegradable membranes are used in dental surgery to treat periodontal defects. The use of these membranes has led to the development of an innovative technique, Guided Tissue Regeneration, GTR [1]. The technique is based on the programmed maintenance of their physical and mechanical properties of these membranes for a fixed period of time and their gradual and progressive degradation. Therefore, the chemical and physical properties of these membranes have to meet stringent requirements.

Membranes made with biodegradable polymers [1,2] are frequently used in the GTR technique. We report a vibrational study on the *in vitro* degradation of a hydroxyapatite-polymer composite membrane. The apatitic component was added to the polymer (poly(ε-caprolactone)-*block*-poly(oxyethylene)-*block*-poly(ε-caprolactone) copolymer, PCL-POE-PCL) by the manufacturer (Fin-Ceramica s.r.l., Faenza, Italy) for its biological behavior: since periodontal membranes are involved in a bone regeneration process, this could be enhanced by the presence of hydroxyapatite, the main component of the inorganic phase of bone.

The composite membrane was studied, by Raman and FT-IR spectroscopies after immersion for different periods of time, at 37°C, in three different degradation media: 0.01 M NaOH aqueous solution, saline phosphate buffer at pH 7.4 and Simulated Body Fluid (SBF) buffered at pH 7.5 [3]. The latter medium was chosen to study the bioactivity of the membrane (i.e. the capability of nucleate on its surface a carbonate and/or apatitic phase).

The vibrational data showed that both polymeric and apatitic components are involved in degradation; the former undergoes preferential degradation of POE component, the latter is removed by the degradation media faster with respect to the polymer. The Raman intensity ratios I_{1050}/I_{1067}, I_{1308}/I_{1281}, I_{1422}/I_{1475} and I_{963}/I_{1726} and the IR intensity ratio I_{2944}/I_{2866} were identified as spectroscopic markers of degradation. The vibrational results were in good agreement with the thermogravimetric data (the destructive thermogravimetric technique was used to determine the percentages of polymeric and apatitic components during degradation). Vibrational spectroscopy appeared to be a valid non-destructive method for investigating the degradation mechanism and the kinetics of the composite membrane, as an alternative to destructive thermal methods.

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P12.12

BIOCHEMICAL CHARACTERIZATION OF HUMAN RENAL TUMORS BY IN VITRO NUCLEAR MAGNETIC RESONANCE

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The applications of in vivo Magnetic Resonance Spectroscopy (MRS) to the study of human renal tumors (1) are recent. Moreover, in vivo MRS allowed a differential diagnosis between prostatic tumor and prostatic hypertrophy (2). Nevertheless, in vivo studies must be preceded by in vitro biochemical results. With this aim, we report the in vitro MRS data obtained from the extracts of human renal tumors after surgical resection.

Samples from 18 patients with nephrocarcinoma and from 5 patients with oncocitoma were examined. In the case of radical nephrectomy fragments of healthy renal parenchyma were also removed.

The healthy and pathological samples were extracted with the aim to obtain the water soluble metabolites owing to the method used by us for brain tissues (3). The extracts were examined by ^{1}H MRS.

The healthy kidney tissue showed a biochemical composition very rech in osmotically active metabolites. They can be considered markers of good kidney function because they are responsible for the cell's osmotic balance in the extracellular environment.

The same metabolites are virtually absent in the MRS spectra of the extracts from nephrocarcinomas and this behaviour can be considered a hallmark of these tumors. On the contrary, some aminoacids as alanine, glycine, taurine and glutamic acid are present in increased amount in the spectra of these neoplastic tumors as confirmed by the High Performance Liquid Chromatography (HPLC) analysis of the aminoacidic fraction.

Apart from disclosing a heterogeneous composition of oncocytomas, the main feature of spectroscopic analysis was demonstration of glycerophosphorilcholine, phosphorilcholine and choline in ratios typical of this benign pathology.

This work investigates the biochemical composition of nephrocarcinomas, oncocytomas and healthy renal parenchyma by in vitro MRS measurements. Biochemical markers typical of neoplastic and healthy tissues can be identified and used, in the future, to characterize these tumors by in vivo MRS spectroscopy.

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HUMAN CANCER PROSTATE TISSUES ANALYZED BY FTIR MICROSPECTROSCOPY AND SRIXE TECHNIQUES

P12.13

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It is known that FTIR spectra of human tissues are specific and can be used to distinguish between various disease states. The human prostate tissues were obtained during surgical operation performed due to cancer disease. In this study cancerous and non-cancerous parts of prostate tissues were examined. Sample sections were mounted onto maylar foils and measurement by Fourier Transform Infrared (FTIR) microspectroscopy and Synchrotron Radiation Induced X-ray Emission (SRIXE) methods. Neighboring sections of the same sample were mounted onto glass slides for histopatological study.

SRIXE is suitable technique for trace element analysis. The two dimensional scans on both cancerous and non-cancerous parts of the tissues were done by SRIXE in order to find trace element distributions. Then the same samples were measured by FTIR microspectroscopy. The spectra were collected in the frequency region from 700 cm^{-1} to 4000 cm^{-1} on Excalibur spectrometer with infrared microscope UMA-500 equipped with an automatic x y-stage and video camera. Both FTIR spectra and elemental distribution show differences between cancerous and non-cancerous parts of analyzed tissues. Correlation between distribution of trace elements and chemical functional groups are discussed.

P12.14

RAMAN SPECTROSCOPY OF ELASTIN-LIKE POLYMERS

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Raman spectra of elastine-like polymer, poly(VPGVG), were measured in H_2O and D_2O at temperatures 25 and 60 °C. Wavenumbers of maxima and shapes of some bands in the spectrum of the solution existing at the lower temperature differ from those of the suspension or of the precipitate formed at the higher temperature. Sufficiently pronounced changes were found in the region of C-H stretching vibrations and also for some Amide and C-H deformation vibrations.
Spectra of the polypentapeptide in water were compared with the spectrum in the solid state and also with the spectra of other peptide compounds. Structures corresponding to the spectral results were proposed.

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STRUCTURAL STUDY OF SOME SPECIFIC ELASTIN HEXAPEPTIDES ACTIVATING MMP1

P12.15

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Elastin, the insoluble polymer of tropoelastin, is responsible for the elasticity of vertebrate tissues. Its degradation by peptidases leads to the production of small peptides of few residues, which can induce very important biological effects notably in the extra cellular matrix area.

In this work, we studied elastin derived peptides, some of them presenting effects onto MMP1 activation and production. These hexapeptides belong to exon 24 in the human tropoelastin sequence (the soluble precursor of the insoluble elastin), with the main one **V G V A P G** (the five others are circular permutations of this one).

We also studied **P G A I P G** (another elastin peptide) and **L G T I P G** which belongs to laminin (another matrix protein).

All these synthetic hexapeptides have been probed in aqueous solution by using electronic circular dichroism spectroscopy (JASCO J-810; far UV spectral range 185 - 250 nm).

They present CD shape spectra rather characteristic of a mixing of turns and disordered conformations. Nevertheless, two spectral groups can be defined in regard of their dominant negative band position. Strikingly, one group correspond to the biologically inactive peptides, and the other to the active ones, which strongly suggest that this MMP1 activation is structure dependant.

All the biologically active elastin hexapeptides were shown to contain the **G X X P G** repetition and more precisely the tetrapeptide sequence **G X X P** which could form a specific β-reverse turn. Using both prediction methods and our sofware COUDES (TURNS), we have shown that the active peptides could adopt a type VIII β-reverse turn and not the inactive peptides. These results agree well with the observed spectroscopic data as the short sequences of 6 residue long, are rather flexible and may adopt different conformation states (mainly turns and random coil).

Further data will be necessary to understand this mechanism in detail, but it is interesting to probe the role of β-reverse onto the peptides structure by molecular modeling and specially by performing a molecular dynamics study in an explicit aqueous solvent. This work is under progress.

Biospectroscopy (3)

-Phamarceuticals

P13.1

EFFECT OF METAL TRANSITION BINDING ON THE TAUTOMERIC EQUILIBRIUM OF THE CARNOSINE IMIDAZOLIC RING

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Transition metal ions play an important role in processes involving free radicals in biological systems. In fact, they can catalyse the formation of reactive oxygen species resulting in oxidative tissue damage. One of the mechanisms by which antioxidants protect targets from oxidative stress is the chelation of transition metals, preventing them from participating in deleterious processes [1].

L-carnosine (β-alanyl-L-histidine), found in skeletal muscle and brain of many vertebrates, has a good potential to act as a natural antioxidant *in vivo* and seems to be involved in modulation of enzymatic activities and chelation of heavy metals. Moreover, carnosine is a substrate for the metal-activated enzyme carnosinase. Consequently, more information on the interaction of metal transition ions with carnosine can aid metal-enzyme studies and shed light on the biological role of this dipeptide.

The ability of carnosine to chelate various transition metal ions was tested by Raman and IR spectroscopy at different pH values. Both the Raman and IR spectra present some marker bands useful for the identification of the complex structure predominating at a specific pH. In particular, Raman spectroscopy appears to be a useful tool for analyzing the tautomeric equilibrium of the imidazole ring of carnosine.

The neutral imidazole group of this dipeptide gives rise to some bands that appear at different wavenumbers, depending on whether the imidazole ring is in the N_τ-H (tautomer I) or in the N_π-H (tautomer II) protonated form [2]. At pH 7 and 9 the molecule exists in equilibrium between the two tautomeric forms [3]. The tautomer I is preferred in the free ligand; the tautomeric preference can be completely upset after the complex formation [3]. The metal coordination site can be monitored by some Raman bands such as the C_4=C_5 stretching bands; for example, upon Cu(II) chelation, the νC_4=C_5 band of the imidazole moiety appears in the 1603 -1587 cm^{-1} region when the N_τ atom of the imidazole group acts as a Cu(II) coordination site, whereas it appears in a lower wavenumber region, 1575-1569 cm^{-1}, when the metal coordination takes place via N_π with N_τ protonated [4].

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P13.2

VARIATIONS OF THE IRON CORE STRUCTURE AND MÖSSBAUER PARAMETERS IN IRON–DEXTRAN COMPLEXES WITH DIFFERENT MOLECULAR STRUCTURE

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Iron–dextran complexes are pharmaceutically important models of iron storage protein ferritin. These complexes are used or elaborated as drugs for treatment of iron deficiency anemias. Ferritin molecule consists of the iron core in the form of a polynuclear hydrous ferric oxide (FeOOH) with about 4500 iron atoms with multisubunit protein shell while iron–dextran complexes consist of a FeOOH core with a dextran shell.

The iron core in a number of iron–dextran complexes as industrial products as elaborated samples with some variations of molecular structure and effect in the body was studied by Mössbauer spectroscopy. Measurements were made at 87 K for the complexes in frozen solution and at 295 and 87 K for lyophilized samples. Mössbauer spectra measured at 87 K demonstrated superparamagnetic, magnetic and paramagnetic states of the iron cores (Fig. 1) while spectra measured at 295 K showed paramagnetic state of the iron core. Moreover, Mössbauer parameters appeared to be different for various iron–dextran complexes at the same conditions (Fig. 2) as well as for one type of complex in frozen solution and in lyophilized form.

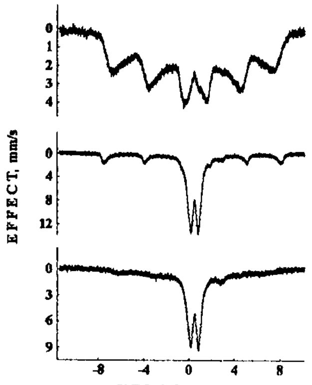

Fig. 1 – Mössbauer spectra of three different iron–dextran complexes at 87 K.

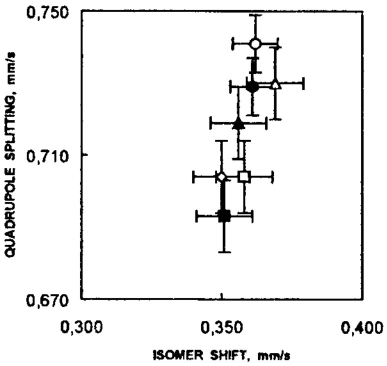

Fig. 2 – Differences of Mössbauer parameters for various lyophilized iron–dextran complexes at 295 K.

Mössbauer parameters of the iron–dextran complexes were analyzed and related to the microstructural variations of the FeOOH cores in various complexes as well as compared with well known data for ferritin molecules.

AB INITIO AND SEMI-EMPIRICAL CONFORMATIONAL STUDIES OF PYRIDOXAL-5'-PHOSPHATE DERIVATIVES

P13.3

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It is known that pyridoxal-5'-phosphate (PLP), the biologically active coenzymic form of the vitamin B_6 compounds essential for many enzymatic reactions, can also modify proteins and influence their functional states and properties. Carbonyl group of PLP interacts with amino groups to produce reversible complexes (Schiff bases) and stable adducts (secondary amines).

Conformational studies for reversible complexes and stable adducts of PLP with amino acids were performed using Hartree-Fock ab initio (3-21G) and semiempirical (AM1, PM3) calculations. Conformational energy surfaces versus torsional angles for PLP complexes with glycine, L-valine, L-tyrosine, and L-tryptophan were calculated with the use of GAMESS. During the structure optimization these torsional angles were fixed and the other parameters varied.

Two conformational states (another two are symmetrical relative to the ring), differed by carboxyl group orientation with regard to pyridine cycle, were found for stable adducts of PLP with aliphatic amino acids (Fig.2). For complexes of PLP with tyrosine or tryptophane situation is more complicated due to interaction between pyridine and aromatic rings.

On the base of computational studies results, photochemical and time-resolved fluorescence data we suggest a possible scheme of excited states deactivation for PLP-amino acid complexes.

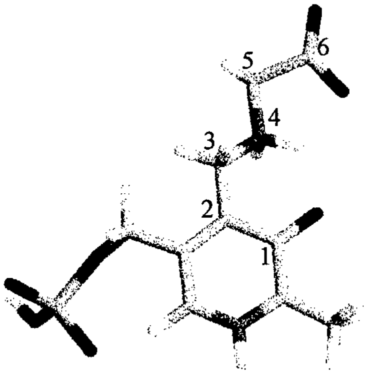

Fig.1. Stable adduct of PLP with glycine.

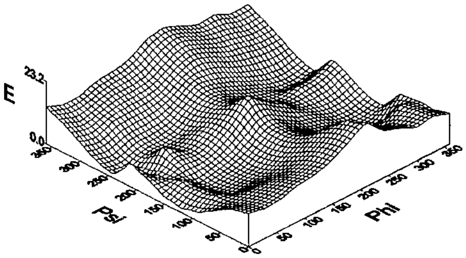

Fig.2. Conformational energy surface versus torsional angles Phi (1234) and Psi (3456) for PLP-glycine stable adduct. Numbers correspond to atoms in Fig.1.

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P13.4

ENCAPSULATION PHOTO-ASSISTED OF AN HALLUCINOGEN IN THE SOL-GEL OPTICALLY TRANSPARENT GLASS AND USED AS ACID AND BASE SENSOR

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Norharman (9H-pyrido[3,4-b]indole) is found as neutral free base form (NN) and monocation form (NH^+), in which the pyridine N is protonated. The spectroscopic properties of norharman have been studied by many authors(1) due to its uses as hallucinogen, and its importance in biological systems as monoaminooxidase inhibidor. Here we realize a detailed study of photophysical properties of norharman species in some hydrophobic and hydrophilic enviroments, considering the solvent, concentration and pH effects. These determinations were used to characterise and to identify the norharman species that is solubilized into the interior of neutral (triton X-100), anionic (dodecyl lithium sulphate) and cationic (hexadecyltrimethyl ammonium bromide) micelles, all of them were prepared under physiological conditions. Finally, the "active species" of norharman was immobilized in the sol-gel optically transparent glass.

Steady-state and time resolved emission spectroscopic techniques at 77K and molecular orbital calculations using AM1-MOPAC/93(2) for geometry optimization and HAM/3-CI(3) for the excitation energies calculations. have been used here. The photophysical properties of all species were determinated and we verified that each one of them displays distinct photophysical properties from one another. For example, in methylcyclohexane, the (NN) monomer was found; in ethanol, the strongest molecular aggregation (self-association) and in 2,2,2, trifluoroethanol (tfe), the monomeric form of the complex formed between (NN) and (tfe) through a hydrogen bond. The solubilization of the (NH^+) in micellar media, indicated, that the micellar region where (NH^+) species are anchored (aqueous or hydrophobic regions) is dependent of the polarity of micelle. The photophysical properties of (NH^+) obtained in gels were compared to those solutions and the encapsulation of (NH^+) in modified sol-gel glass produce a optically transparent and quite durable gel with drug-surface interaction reduction and the new glass was tested as a sensor of the acid and basic media due deprotonation dynamic of the (NH^+) species when it is in contact with hydrophobic medium.

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SOLVENT AND pH EFECTS ON THE PHOTOPHYSICAL PROPERTIES OF CHLORPROMAZINE SPECIES

P13.5

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Steady-state and time resolved emission spectroscopic techniques at 77K and molecular orbital calculations using AM1-MOPAC/93(1) and ZINDO/S-CI(2) have been used to study the (2-chloro-10-[3-dimethylamino-propyl]phenothiazine hydrochloride); chlorpromazine or (CPZ^+), in the monocation form, in different environments. In aqueous medium the monomer species of (CPZ^+) were determined, in ethanol. The monomeric form of the complex, formed between the free base form (CPZ) and ethanol, through bonded hydrogen (CPZ-H) was determined, and in H_2SO_4 0.5N, the dication (CPZ^{++}) was found. The photophysical properties of all species were determined and we verified that each one of them displays distinct photophysical properties from one another. For example, (CPZ^{++}), at the lowest electronic singlet state S1 (n,π^*), with energy 5.246 eV and at the lowest electronic triplet state T1 (π,π^*) with energy 3.848 eV and is the first order spin-orbital coupling. A different behaviour in the phosphorescence emission of the (CPZ^+) as a function of pH. Species was observed. In aqueous solution a discontinuous transition occur when the equilibrium is shifted from one species to the other. In the pH range from 0.6 to 4.0 the (CPZ^{++}) are present, while from 6.0 to 8.0 (CPZ^+) is dominant. Finally we observed that the internal heavy-atom effect is important to the determinations of the photophysical properties of each species of (CPZ^+)

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P13.6

FT-IR AND RAMAN SPECTROSCOPIC STUDIES OF TIMOLOL MALEATE METAL SALTS

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Timolol is a widely used anti-hypertensive drug as a $\beta_1$and β_2 non-adrenergic inhibitor (β-blocker) of catecholamines. The drug reduces the blood pressure and headaches caused by hypertension, in particular it is used for the treatment of glaucoma.

The FT-IR spectra of timolol maleate were obtained in lipophilic solvents, such as chloroform and carbon tetrachloride solutions. In these solvents two bands were observed in the hydroxyl absorption region at 3400 and 3270 cm^{-1}, which are assigned to the free and hydrogen bonded vibrations of –OH and amino group. In the region of 3000-2800 cm^{-1} were observed the characteristic stretching vibrations of $-CH_3$ and $-CH_2$- groups. The carbonyl absorption of maleate was located at 1690 cm^{-1}. In the presence of calcium cations there were slight changes in the stretching and bending vibrations of $-CH_3$ and $-CH_2$-absorptions, as well as in the C=C band of maleic acid stretching vibration of C-N. The band near 854 cm^{-1} changes also shape and intensity in the Raman spectra of aqueous solutions as well the $-CH_3$ and $-CH_2$- bands.

In conclusion the FT-IR and Raman spectra of timolol indicate its vibrational behaviour in lipophilic region of the cell membrane in such a way to obtain a conformation which inhibits the opening of Ca^{2+} and Na^+ channels, which otherwise would lead to hypertension.

PHARMACOLOGICAL EFFECTS ON BRAIN: FT-IR RESPONSE

P13.7

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An important problem of recent pharmacological interest is surely represented by the possibility to reveal substances which are able to get over the haematic-encephalic barrier and hence eventually to recover or damage the brain. The monitoring of drugs distribution by means of traditional and usual methods can result quite difficult because of the necessity to use radioactive tracers.

In the present work we performed a Fourier Transform Infrared (FT-IR) analysis on rat encephalon samples in the CH-OH vibrational stretching region (2400 - 3800)cm^{-1}, in order to reveal the presence of a commercial and very diffuse benzo-diazepam ($C_{16}H_{13}ClN_2O$) (see Fig.1).

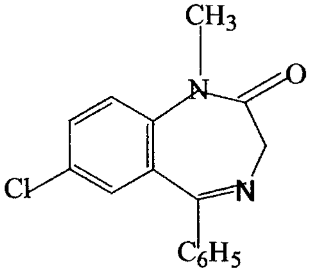

Fig.1 - Diazepam

This substance was administrated in doses consistent with rats weight. From a first qualitative analysis in the studied frequency range, the comparison between the spectral feature of normal brain and the one with administrated diazepam has unambiguously showed that the CH stretching region seems not to suffer any change for the pharmacological treatment, as we expected, instead the OH band is strongly modified due to the presence of a contribution centered at about 3500 cm^{-1}, which is characteristic of diazepam molecule. Of course the IR absorbance spectrum of pure diazepam was performed and analysed as well.

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P13.8

A SPECTROSCOPIC INVESTIGATION OF THE CU(II)-CAPTOPRIL SYSTEM

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Captopril (CpSH), a synthetic 3-mercapto-2-methyl-propionyl derivative of L-proline, is an angiotensin converting enzyme inhibitor and is currently one of the drugs most widely used in the treatment of arterial hypertension and congestive heart failure [1]. Since post-ischemic myocardial dysfunction mobilises metal ions such as Cu(II) which can catalyse the formation of reactive oxygen species able to produce oxidative damage [2], the beneficial action of CpSH could be connected with its ability to bind Cu(II) and to transport it across the cell membranes. To gain more insight into the interaction of CpSH with Cu(II) ions, a study of CpSH in the absence and presence of Cu(II) at different pHs was carried out by some spectroscopic techniques.

The NMR investigations showed the interconversion between the trans and cis conformations by rotation around the amide bond; This interchange is of interest in the study of the CpSH-enzyme interaction [3].

The vibrational data confirm the ability of CpSH to form a complex with the reduced Cu(I) [4]. In fact, the presence of copper (II) induces some significant changes in the CpSH Raman spectra, suggesting the formation of a dithiol species, CpSSCp, as well as the coordination of CpSH with Cu(I). The formation of the CpSSCp species is due to a redox reaction of Cu(II) with CpSH.

As far as the formation of a CpS-Cu(I) complex is concerned, CpSH can coordinate metal ions *via* three possible sites: the thiol sulphur, the carbonyl oxygen and the carboxylate oxygen. The involvement of the COO^- group in copper chelation is affected by pH.

The spectroscopic results identify the CpSH sites involved in the copper complex (CpS-Cu(I)) and characterize its structure, supporting the possible antioxidant mechanism of action of this molecule.

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IR-SPECTROSCOPIC STUDY OF LEVAN FERMENTATION

P13.9

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Levan is poly-D-fructan, extracellulary produced by different bacteria. It is viscous, biologically active, non-toxic, with a unique structure and extraordinary properties. Levan can be used as thickener or stabiliser in the food, pharmaceutical and cosmetic industries and is good raw material for fructose production. Biological activity of microorganism-produced levan predicts its applicability in medicine as a non-specific immunostimulator with antitumour and antiinflammatory properties, as plasma volume expander and prolongator of the effect of drugs (1).

The aim of this study was to apply infrared spectroscopy methods for levan fermentation monitoring, levan precipitation control and sediment chemical composition investigations.

Inoculated in glucose medium at 30°C *Z. mobilis* 113 "S" produces 30-50 g/l of levan during batch or continuous fermentation. After biomass centrifugation levan was precipitated with 75% ethanol. Lyophilised samples were dried, milled, tabletted with KBr and their mid-IR absorption spectra in the fingerprint region were registered. Qualitative and quantitative analysis of the microbial biomass, cell free fermentation culture liquid and precipitated levan complex was carried out. The principal components of microbial biomass are carbohydrates, nucleic acids, proteins and lipids. The concentration of those components in all samples was evaluated from the mid-IR absorption spectra according to (2), using as characteristic absorption bands: 1080 cm^{-1} (COC valent vibrations in cyclic structures) for total carbohydrates, 1250 cm^{-1} (phosphate group), 1660 cm^{-1} (Amide I) for proteins and 2930 cm^{-1} (streching asymmetric vibrations of CH in methylene group) for lipids.

Investigations of IR-spectra of the samples showed that bacterial biomass of *Zymomonas mobilis* before fermentation - at late exponential growth phase is characteristic with high protein - 54.5 % dw, and nucleic acid - 18.5 % dw content and low total carbohydrate concentration - 17.1 % dw. In the absorption spectra of fermentation culture liquid, centrifuged at 16.000 rpm, were not detected main bacterial cell components, but "ammonium" band at 1410 cm^{-1} testifies the presence of incubation media components. Dominating component in the sediment is fructose polymer with negligible content of other oligosaccharides, that proves purity of the precipitated leven sediment.

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P13.10

NEW RIFAMYCIN DERIVATIVES WITH A 4-PIPERIDONE SUBSTITUENT AT C(3)

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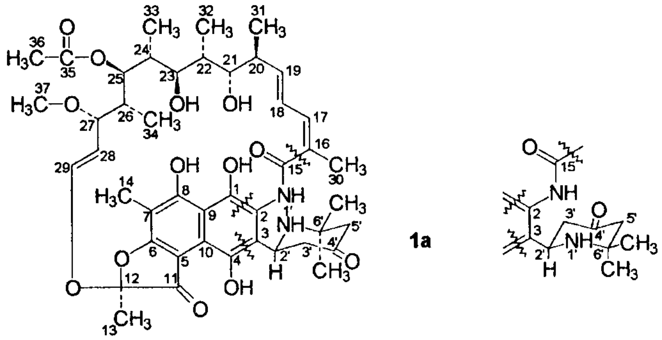
Rifamycins are antibiotics especially useful in therapy of tuberculosis and other diseases caused by pathogenic *mycobacteria*. Due to worldwide propagation of tuberculosis during last decades, the study on new potential drugs is the matter of growing importance.

A new group of rifamycin derivatives with the 4-piperidone substituent at C(3) revealing biological activity has been obtained [1]. The subject of presented project was the determination of the structure of new derivatives by spectral methods.



1a **1b**

Fig. 1. Structures of newly obtained compounds

In the structural study the NMR advanced techniques were applied, as (1D) and (2D) ^{1}H-NMR and ^{13}C-NMR-spectra, including correlation ^{1}H,^{1}H COSY and ^{13}C,^{1}H COSY. The MS-HR spectra were also helpful. Results have been related to the spectral data published for other rifamycins [2].

It was confirmed that the new compounds **1a** and **1 b** are diastereomers (Fig. 1). Furthermore, tautomerism between positions 8 and 11 was noticed, as well as hydrogen bonds between amide nitrogen at C(2) or oxygen atom at C(4) and 1'-NH proton, stabilising the isomers **1a** and **1b**, respectively.

To search for derivatives exhibiting higher antibacterial activity the major isomer **1a** is used as substrate for further modification [3].

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VIBRATIONAL SPECTROSCOPY OF GLUTETHIMIDE AND ITS DERIVATIVES

P13.11

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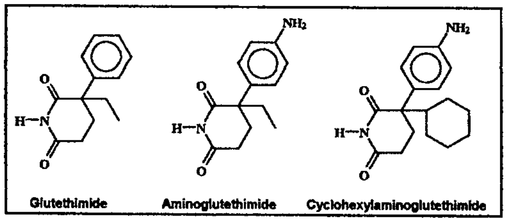
Glutethimide (G) is a known non-barbituric sedative or hypnotic drug. Aminoglutethimide, a derivative of glutethimide, (AG), is used as an efficient agent for the treatment of advanced breast cancer in post menopausal women. Cyclohexylaminoglutethimide, another derivative of glutethimide, (CHAG) is a potential nonsteroidal drug for the treatment of estrogen-dependent breast cancer.



The studied molecules contain a common cyclic imide fragment that seems to be particularly sensitive to specific intermolecular interactions. Here we use vibrational spectroscopy to study these interactions.

The vibrational spectra of G, AG and CHAG molecules were studied in low-temperature Ar and N_2 matrices and CCl_4, $CHCl_3$, CS_2 and CH_3CN solutions (at different concentrations). It was found that increasing the solute concentration in CCl_4, CS_2 and $CHCl_3$ solutions leads to a formation of dimers. On the other hand, in CH_3CN solution only the solute-solvent complexes occur.

The molecular structure and theoretical IR and Raman spectra of G, AG and CHAG were predicted with the use of the ab initio RHF/6-31G** and density functional B3LYP/6-31G** quantum mechanical methods. A comparative analysis of theoretical and experimental spectra of monomeric (isolated) species has led to the assignment of most of the absorption bands in terms of G, AG and CHAG normal modes.

The IR and Raman spectra of crystalline samples (solid film and KBr pellet) were recorded as well. A reliable assignment of the IR and Raman spectra of crystalline G, AG and CHAG was obtained with the help of theoretically simulated spectra and the previous results of simpler model systems.

We found that :

1. G, AG and CHAG dimers are bound by a pair of hydrogen bonds involving the imide NH and C=O moieties forming a cyclic structure.
2. The amino $-NH_2$ group of AG and CHAG is involved in weaker hydrogen bonds than the imide NH moiety.
3. G, AG and CHAG exhibit very similar spectral patterns, especially in the region of imide N-H and C=O stretching vibrations.
4. The Raman solid state and solution spectra are similar and should not be recommended to monitor interactions with the environment.

P13.12

REGIOSELECTIVITY IN THE *O*-METHYLATION OF ERYTHROMYCIN A OBSERVED FOR NEW PROTECTING SUBSTITUENTS

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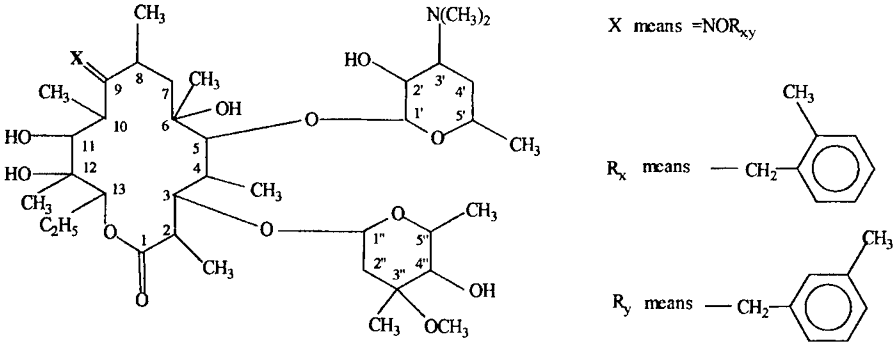
Erythromycin A is widely used in the control of Gram-positive bacteria, and its 6-*O*-methylated derivative, clarithromycin, is the remedy of choice against the stomach ulcer caused by *Helicobacter pylori*. During methylation competitive substitution in the 6-*O* and 11-*O* positions is observed, and in erythromycin A favored is the undesirable 11-*O* substitution. However, in the erythromycin A substituted by 9-[*O*-(2-chlorobenzyl)oxime] the yield of clarithromycin is 83% [1].



We examined the regioselectivity of methylation process after substitution of the position 9 by *O*-(2-methylbenzyl)oxime and *O*-(3-methylbenzyl)oxime. In the ^{1}H NMR the spatial interaction between the 6-*O*-methyl group and the benzyl substituent was noticed, causing magnetical nonequivalence of the geminal benzyl protons. Nevertheless, some improvement in the yield (over 85%) of 6-*O*-methylation was observed in case of substitution of the position 9 by $R_{x,y}$ as compared with results described in [1], indicating close contacts between substituents in positions 9 and 11.

To elucidate the steric interactions of the $R_{x,y}$ substituents with the hydroxyl groups in positions 6 and 11, molecular quantum mechanical modeling using semiempirical PM3 method has been performed. The parent X-ray structure of erythromycin A has been derived from the Cambridge Structural Database [2], and after introduction of proper substituents the structure was optimized. Explicit shielding of the 11-OH proton was observed, the distances to substituents R_x or R_y being in the range 1.7-1.8 Å. In case when the methyl substituent in $R_{x,y}$ was replaced with chlorine, respective calculated distances were 2.7 and 3.0 Å, thus, the shielding was less effective. Moreover, discernible weaker interactions were found between $R_{x,y}$ and 6-OH; the respective distances were 4.2-4.6 Å. The calculated rotation barriers for O–$R_{x,y}$ were 16 kJ/mol.

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HYDROGEN BONDS IN THE HYDROXYLATED CEPHALOSPORIN SYSTEM INVESTIGATED BY ^{1}H NMR AND X-RAY

P13.13

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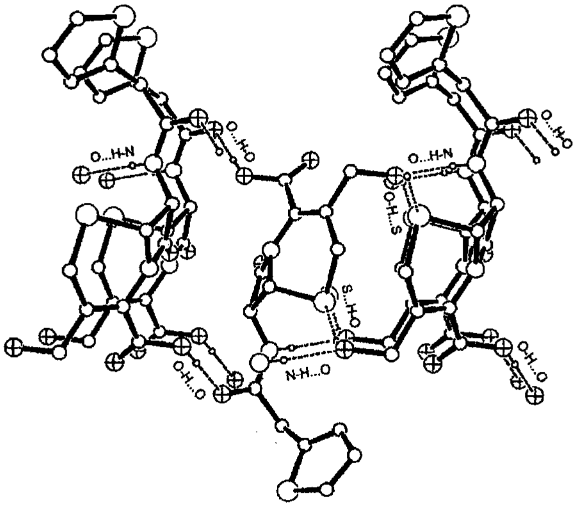
Cephalosporins are widely used broad-spectrum antibiotics, exhibiting antibacterial activity against both Gram-positive and Gram-negative bacteria. In human after parenteral administration of Keflin (Seffin) the metabolite 7-[(2-thienylacetyl)-amino]-3-desacetyl-cephalosporanic acid (A) is formed which discloses only trace activity as compared with the parent drug. It was found by NMR and IR [1] that in solutions the free hydroxyl group in (A) can form intramolecular hydrogen bonds and in this manner protect the carboxyl substituent. In general, blocking of the carboxyl group in cephalosporins results in lowering or decay of antimicrobial activity [2].

In contrast, in the crystal lattice of (A), strong intermolecular hydrogen bonds, in which the peptide moiety is engaged, have been observed by X-ray. The molecules are arranged in form of parallel helices oriented along the b axis stabilized by O–H...O bond between the carboxyl and peptide carbonyl groups (O–O distance 2.63 Å). The peptide imino and hydroxymethyl groups form the other hydrogen N–H...O bonds (N...O 2.85 Å). The interactions in the lattice are shown in the Scheme.



Above results of the crystallographic study revealed only intermolecular close contacts of the hydrogen bond nature in the crystal lattice of (A). Thus, the intramolecular interactions observed in solutions are not formed in the solid state.

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P13.14

STRUCTURAL STUDY OF A NEW 1-METHYLPYRAZOLIN-BIS(TRICARBONYLIRON) COMPLEX BY ^{1}H NMR AND X-RAY. PROTON SIGNAL ASSIGNMENTS BASED ON COUPLING CONSTANTS AND CRYSTAL STRUCTURE

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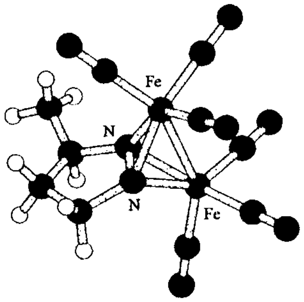
In the reaction of acetaldehyde azine $CH_3CH=N-N=CHCH_3$ with triiron dodecacarbonyl instead of expected bis-aldoiminato complex [1] a new methylpyrazolin-bis(tricarbonyliron) compound has been obtained as result of cyclization of the ligand with a proton-rearrangement during complexation [2]. Similarly as in ketoiminato complexes [3] the central core of this product consists of an almost symmetrical tetrahedron comprised of two iron and two nitrogen atoms, but in contrast to the named compounds the nitrogens are connected by a σ-bond.



In the methyl substituted pyrazolin ring 6 groups of nonequivalent protons with 9 different coupling constants were observed. First after the geometry of the complex was clarified by the crystallographic X-ray study the assignment of multiplets to the hydrogen atoms in particular positions could be accomplished, basing on the Carplus relation. The observed coupling constants varying from about 2 until 13 Hz, were correlated with the torsion angles H'-C-C-H" determined by X-ray. Consequently, the assignment is as follows: 1-H, 3.52 (in ppm, δ); 2-H_a, 2.75 (the index *a* means the position *anti*, whereas *s* is *syn*, with respect to the 1-CH_3 group); 2-H_s 2.40; 3-H_a 3.35; 3-H_s 3.65. The doublet of the methyl group appears at 1.30 ppm. The long range couplings over more than 4 bonds were neglected.

Above assignments were possible by complementary application of NMR and X-ray analysis.

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SPECTRAL INVESTIGATIONS OF SOME POWDER DRUGS WHITE COLOR

P13.15

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The research work presented within this paper aimed to offer a quantitative spectral insight on the white of some semi-synthesis products used in medical treatment. This physical feature of white drug powders intended for sterile injection represents a ubiquitous parameter in international pharmacopoeia statements but only qualitative evaluation is provided by now.

Our study was based on light re-emission measurements at the smooth surface of drug sample in three spectral ranges: blue, green and red as well as in white light, in comparison with standardized white glass controls. We tested over one thousand antibiotic batches representing penicillin and penicillin derivatives but also some other different white antibiotic powders. Not only recently yielded batches but also six or twelve months old ones were taken into study.

Statistical analysis was carried out by means of a modern graphical method, suitable for comparative studies, in order to establish numerical coordinates able to be used for quantitative evaluation of drug powder white color - the "white degree" parameter.

In the same framework re-emission, measurements could be used not only for the characterization of white drug powder aspect and purity but also for their validity term when imposed aging tests are accomplished.

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P13.16

UV-VIS STUDY ON ANTIOXIDATIVE PROPERTIES OF SOME PHENOLIC ANTIOXIDANTS

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The following paper reports a spectrometrical UV-VIS study on the antioxidative properties of some phenolic derivatives which could be considered as major exogenous antioxidants (Aox) against lipid peroxidation: D-α–tocopherol, D-α-tocopheryl acetate (E vitamers) and t-butylhydroxytoluene. The study was developed knowing that a potent radical-scavenger reacts rapidly with a stable free radical (FR) like 2,2'diphenyl-1-pycrilhydrazil (DPPH) [1].

The UV - VIS experiments were tackled at different molar ratios Aox:DPPH, ranging between 1:1 up to 1:5, in protic organic media. The molar ratio was chosen according to the exhibited limits of tocopherol antioxidant activity against the DPPH free radical. The data obtained by using the UV -characteristic signal of the investigated compounds (λ_{max} = 294 nm for a-tocopherol, i.e.) allowed the elucidation of some kinetic aspects of antioxidative reaction performed in systems *in vitro* a-like. It was proved that E vitamers exhibit a combined reaction order (1 and 1.5) on the investigated domain of molar ratios.

Using as marker of antioxidative activity the constant rate of phenolic compound reaction with the stable free radical (i.e. for α-tocopherol k_i was ranging between 1×10^{-3} and 2.52×10^{-4} mol $^{-1}$ s^{-1}, depending on the used Aox:FR molar ratio) it was proved that the order of antioxidative power for the investigated compounds is: α-tocopherol> α-tocopheryl acetate ≅ t-butylhydroxytoluene, the same with that obtained with biological methods [2].

In this respect the procedure carried out seems to be appropriate for a model of antioxidant power estimation against 2,2-diphenyl-1-picrylhydrazyl free radical.

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IR SPECTRA OF PARACETAMOL AND PHENACETIN. EXPERIMENTAL STUDY AND AB INITIO CALCULATIONS

P13.17

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Para-acet-amino-phenol (paracetamol) and para-acetyl-phenithidyne (phenacetin) are important drugs. Their properties attract much attention, and spectroscopy may serve as an important tool not only for characterizing the samples, but also in achieving a better understanding of the interrelation between molecular and crystal structures and the properties of the compounds.

IR spectra of the title compounds were investigated in the solid state and in solutions; in the solid state also at high pressures up to 4.0 GPa. For paracetamol, the two plymorphs (monoclinic and orthorhombic) were compared. Ab-initio (DFT) calculations of the structure and spectra of free paracetamol and phenacetin molecules were carried out to interpret the spectra.

Calculated vibrational spectra of paracetamol and the phenacetin were compared with experimental data. Ab initio frequencies of both free molecules were close to those in the spectra, which were experimentally measured for diluted solutions in $CDCl_3$. This fact allowed us to conclude that the calculated molecular parameters and force constants correspond to the real ones of the free molecules. Spectral regions characteristic for the definite fragments of the molecules were identified on the basis of the normal coordinate analysis.

Spectra of the solutions differ from the spectra solid crystalline phases. The difference was attributed to the presence of strong hydrogen bonds in the molecular crystals. Spectral manifestations of intra molecular hydrogen bonds O- -H----O=C and N-H----O=C in paracetamol and N-H----O=C in phenacetin crystals were analyzed.

Calculated molecular parameters (bond lengths, valence and dihedral angles) of free molecules were compared with the experimental values of the crystalline forms of paracetamol and phenacetin. This allowed us to determine the difference in the parameters originating from the hydrogen bonds formation

The presence of anharmonic frequencies in experimental IR spectra was pointed out. Region of overtone spectra was registered in the near infrared spectra.

The effects of high pressure on the IR- spectra were interpreted, in relation to the direct single crystal X-ray diffraction data on the structural changes induced by pressure in the crystal.

P13.18

RAMAN SPECTROSCOPY STUDY OF TECTOMER, NEW TYPE OF ANTIVIRAL COMPOUNDS

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We present here the results of Raman spectroscopy study of new type of specific ligands "tectons", fig.1., perspective anti-viral inhibitor - multivalent receptor analog. Tectons demonstrate the effect of self-association, on which the non-covalent complexes are formed.

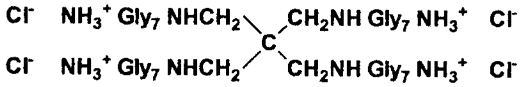

Fig. 1. Chemical structure of tecton.

The structure of associated tecton complexes (called tectomers) is not clear now. This paper describes our results of Raman scattering and infrared spectroscopy study of tectomer.

Raman spectra of tecton mainly contains the lines arose from polyglycine chains vibrations. Analysis of amide I and amide III regions of Raman and IR spectra reveals that unordered structure of polyglycine chains is characteristic for tectons. Raman spectrum of tectomers contains set of spectral lines (886, 1031, 1263, 1382, 1424, 1654 cm^{-1}). Their positions, forms and relative intensities are the same with the lines of Raman spectrum of polyglycine II [1]. Polyglycine II structure is characterized by a hexagonal array of helices with threefold screw axis symmetry. Each chain is intermolecularly linked to its six nearest neighbors via hydrogen bonds.

Molecular mechanics simulation (MM+ method was used) gives a number of minimal energy configurations of tectons. The configuration of tecton, which is able to associate and to form the polyglycine II array, is shown on fig.2.

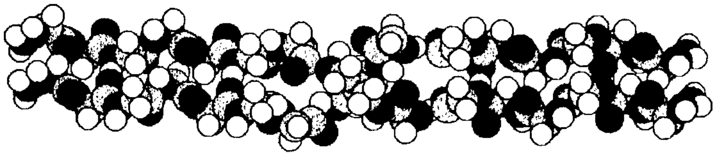

Fig.2. Model of tecton - fragment of tectomer.

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STRUCTURAL STUDY OF SOME (±) 3-ACYLOXY-1-AZABICYCLO [2.2.2]OCTANE-3-CARBOXYLIC ACID HYDROCHLORIDES

P13.19

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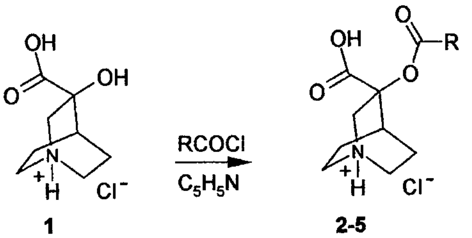
In connection with our interest in the binding mechanisms at neuronal nicotinic receptors we have undertaken a study of some esters derived from (±) 3-hydroxy-1-azabicyclo[2.2.2]octane-3-carboxylic acid hydrochloride,**1**. In these conformationally restricted compounds **1-5** fixed conformations of the flexible δ-aminovalerianic (DAVA) and 3-aminopropionic (3-APA) acids and choline can be mimicked.



R = p-F-C_6H_4 (**2**); p-Cl-C_6H_4 (**3**); 3,4,5-(OCH_3)-C_6H_2 (**4**); $CH(C_6H_5)_2$ (**5**)

Bearing in mind the importance of conformational effects in the ligand-biological receptor interaction we have focused our attention on the role of the acyloxy and carboxylic groups in the 3-position of the 1-azabicyclo[2.2.2]octane (quinuclidine) system. We report the structural study of derivatives **1-5** by NMR spectroscopy, and the crystal structure of (±) 3-diphenylacetoxy-1-azabicyclo [2.2.2]octane-3-carboxylic acid hydrochloride, **5**. The unambiguous assignment of all bicyclic proton and carbon resonances was achieved by the combined analysis of the ^1H-^1H COSY, NOESY and ^1H-^{13}C correlation spectra.

X-ray and NMR data account for the same conformational preferences of the carboxylic and acyloxy moieties. An spatial arrangement in which both carbonyl groups are practically in perpendicular planes might be proposed, both in solid state and in CD_3SO solution.

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P13.20

ADSORPTION OF ANTIMALARIAL DRUG QUINACRINE ON SILVER SURFACE STUDIED BY SURFACE-ENHANCED RAMAN SPECTROSCOPY

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Quinacrine (QA) is an acridine derivative capable to interact with nucleic acids via an intercalating mechanism. Since this drug displays a high sensitivity to the structural and DNA base composition, it has been widely employed in many biophysical studies as molecule probe. One of the most interesting structural features of QA is the possibility to exist under different protonation states, due to the presence of three N atoms in the molecule. This fact allows the use of QA as a molecule probe to investigate the interfacial properties of the silver surfaces employed in surface-enhanced Raman spectroscopy.

In this work, we have studied the adsorption of QA on citrate silver colloids at different experimental conditions: pH, surface adsorbate coverage, Cl^- concentration and excitation wavelength.

The results derived from this research indicates that the second pK of the molecule is markedly lowered in the presence of the surface. This can be adscribed to the adsorption of QA on the silver colloidal surface through two different mechanisms involving either the endocyclic N atom, and the exocyclic N atom linked to both the acridine moiety and the QA side-chain. Moreover, these two mechanisms are related to the existence of different binding sites on the metal surface.

We have compared the results obtained with QA with those obtained from 9-aminoacridine, another acridine derivative which is able to interact under two molecular forms: amino and imino. In the case of QA the interaction seems to take place through the mono or diprotonated forms, and this implies a change of the adsorbate orientation which can be monitored by the ν(C-H) modes sensitive to the adsorbate orientation.

Furthermore, this SERS study is a preliminary investigation conducted for QA with the final objective to study the interaction of this drug with nucleic acids of variable sequence.

VARIATIONS OF THE VIBRATIONAL SPECTRA OF 5'-GMP.Na_2 AND 5'-CMP.Na_2 DUE TO THE RECRYSTALLISATION OF THE COMMERCIAL SALTS IN WATER SOLUTIONS

P13.21

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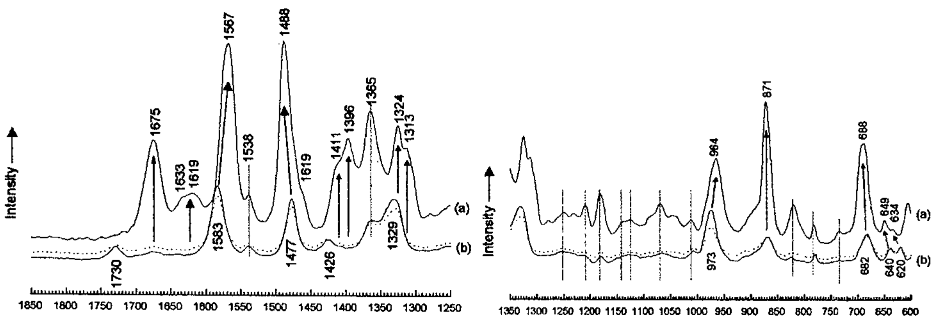
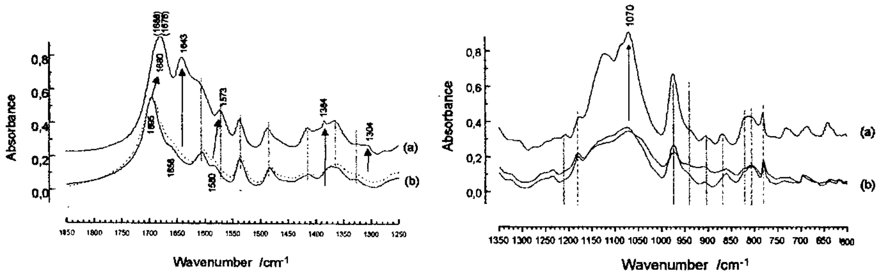
Important variations in the disodium 5'-GMP vibrational spectra have been observed produced solely by dissolving the commercial salt in water and recrystallising it (Figure 1). These changes has been analized and interpreted.The variations are not significant in the disodium 5'-CMP case. It is important to take this information into account before carrying out vibrational studies with molecules of this type, since, for instance, isotopic substitutions may give rise to false isotopic shifts, *i.e.* this may be a result of manipulation of the nucleotide (dissolving and recrystallisation) instead of the isotopic substitutions.



Raman (1850-1250 cm^{-1})

Raman (1350-600 cm^{-1})



IR (1850-1250 cm^{-1})

IR (1350-600 cm^{-1})

Fig 1. Variations in the IR and Raman spectra of 5'-GMP in solid state with re-crystallisation. (a) 5'-GMP commercial; (b) recrystallised forms (normal line=pH 8; dashed line= pH 7).

P13.22

APPLICATION OF LASER SPECTROSCOPY TO THE STUDY OF ALKALOIDS WITH BIOLOGICAL ACTIVITY

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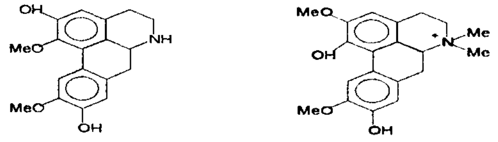
Laser spectroscopy provides a unique and sensitive approach to reveal the physical and chemical properties of biological specimens. The ability to carry out optical and spectroscopy measurements of drugs distribution on cell without foreign markers is important because minimize any possibility of perturbation induced by outside agent or interaction with the normal native cellular environment.

In this work we present the study a preliminary study of the application of laser spectroscopy to the study of alkaloids isoquinolinic and piridinic type with biological activity in mammalian cells.

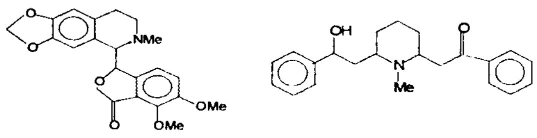
The molecular Fluorescence and Raman spectroscopy using cw Ar and Nd:YAG lasers were used. The alkaloids select for this study were: isoquinolinic (Boldine [I], Laurifoline[II] and Hidrastine [III]) and piridinic (Lobeline [IV]), these compounds shows an important applications in cancer and Leishmanisis treatment.

The Fluorescence and Raman spectra of these alkaloids are reported and compared to those obtained for mammalian cells in vitro in order to study the potential application of these techniques in the spatial distribution of the drugs into cells and tissues without foreign markers.



Boldine(I)

Laurifoline(II)



Hidrastine(III)

Lobeline(IV)

Figure 1. Structure of alkaloids

PRINCIPAL COMPONENT ANALYSIS OF NMR H^1 DATA OF ANTI-INFLAMATORY COMPOUNDS

P13.23

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Recently, our group designed, synthesized and characterized through spectrometric methods, new drugs (see Figure 1) showing biologic activity at arachidonic acid cascade enzyme levels. In the characterization NMR ^1H represents, of course, the most important technique.

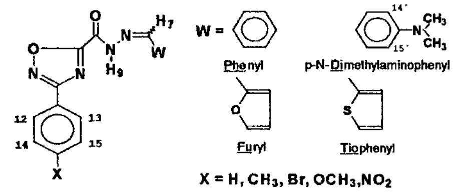

Figure 1

In this work, a data matrix composed of p=20 objects (compounds) and n=4 variables (NMR H^1 peaks $\delta H_{14,15}$, $\delta H_{12,13}$, δH_9 and δH_7) has been analyzed using the chemometric multivariate technique Principal Component Analysis (PCA).

Figure 2 shows the score plot of PC1 (75,7%) against PC2 (13,1% of the variance). PC1 seems to grossly separate X, in negative (OCH_3 and CH_3), positive (Br and NO_2) and in a nearly zero score (H). This is very reasonable since the coefficient of $\delta H_{14,15}$ dominates the PC1 equation.

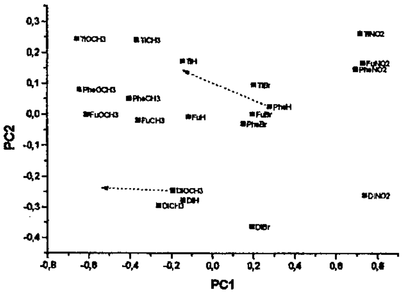

Figure 2

$$PC1 = 0.982\ \delta H_{14,15} + 0.183\ \delta H_{14,15} + 0.003\ \delta H_9 - 0.030\ \delta H_7$$
$$PC2 = -0.040\ \delta H_{14,15} + 0.214\ \delta H_{14,15} + 0.781\ \delta H_9 + 0.585\ \delta H_7$$

If the compounds indicated by dot-arrows were further left in Fig. 2, a perfect separation in PC1 of the different groups (X) should be possible. Indeed, it was this observation that lead us to a more careful analysis of the original NMR assignments in the data matrix. Two mistakes were indeed found. i) A switch in the assignments of $H_{14,15}$ and $H_{14',15'}$ for compound $DiOCH_3$, ii) the 300 MHz spectrum of PheH (as opposed to the original 100 MHz one) with improved resolution gave new values for $\delta H_{14,15}$ and $\delta H_{12,13}$. A new PCA using the new δ values gave similar PC equations and a score plot with $DiOCH_3$ and PheH in positions as predicted above. Thus, we suggest PCA as an alternative way for verifying NMR H^1 assignments of analog compounds.

P13.24

STRUCTURAL AND CONFORMATIONAL STUDIES OF IODO-HISTAMINE

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The iodo derivatives of histamine which contain ^{125}I radioisotope, have been used for many years as isotope-carriers in RIA systems. The growing interest for the use of the iodo-histamine for preparing *in vivo* applicable radiopharmaceuticals, needs investigations on the iodo-histamine structure and the substituent influence on the structure stability and behaviour in biological systems to be undertaken.

The main objectives of our studies were experimental and theoretical indication of the most privileged position of the iodine substitution into the imidazole ring of histamine, as well as investigation of iodine atom influence on the iodo-histamine conformations.

None-radioactive iodo-derivatives of histamine were prepared based on previously described methods, and were purified by crystallisation and HPLC techniques. Mass spectrometry technique (EI and APCI ionisations; Finnigan MAT Mass Spectrometer) has been applied for checking over the products. The structures of the separated isomers of iodo-histamine were determined by ^{1}H, ^{13}C NMR and 2D NMR techniques (D_2O; Varian INOVA 500 MHz NMR spectrometer). The conformations of the most stable tautomers of the iodo-histamine cationic form were investigated by application of the *ab initio* the Møller-Plesset (MP2) molecular orbital calculations, carried out with the GAUSSIAN 94 system of programs, and using the split valence 3-21G** basis set.

Mass spectrometry analysis showed that carrying out histamine iodination with five molar excess of histamine over the iodine (I_2), conducts to the formation of mono-iodo-histamine and ca. 10-15% of di-iodo-histamine. The results of NMR studies supported expectation that 4-I-Histamine (4-I-imidazole-5-ethanamine) is a dominant and the most stable form of iodo-derivative of histamine. The most stable tautomer of 4-I-Histamine cationic form has been predicted, and the potential energy surface has been calculated using the ab initio MP2/3-21G** method.

Both experimental and theoretical methods support that 4-I-Histamine (4-iodo-imidazole-5-ethanamine) is the most stable form among the iodo-derivatives of histamine substituted in the imidazole ring. The most probable explanation of its higher stability is a considerably lower positive charge on C-4 atom in the imidazole ring compared to C-2 atom. This arises from the induction effects of both neighbouring nitrogen atoms that result in a lower electron density on the C-2 atom, and in consequence, lower stability of an intermediate complex with the iodine cation.

Theoretical Spectroscopy

SELECTION RULES FOR THE CHARGE TRANSFER ENHANCEMENT MECHANISM IN SERS: DEPENDENCE OF THE INTENSITIES ON THE L-MATRIX.

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One of the most relevant applications of electronic spectroscopy concerns the determination of the equilibrium geometries of a molecule in its excited electronic states. In the resonant Raman effect, that information comes from the well known Tsuboi's rule (Franck-Condon A-term) [1], according to which, the most enhanced Raman bands are related to the differences between the molecular geometries in the electronic states involved in the resonant process. The Raman intensity of the i-mode with frequency w_i is proportional to those geometrical differences through the Peticolas' equation [2]:

$$I_i = k\, \Delta Q_i^2 w_i^2 \qquad \text{(I)}$$

Where ΔQ is the shift between the minima of the potential energy surfaces of the involved electronic states along the i-mode. In turn, ΔQ is related to the geometrical differences expresed as a function of the internal coordinates acording to [3]:

$$\Delta Q = L^{-1}\, \Delta R \qquad \text{(II)}$$

Where L^{-1} is the inverse of the vibrational normal modes matrix L, obtained by solving the Wilson's equation $GFL = L\Lambda$. Equation (II) shows the dependence of the geometrical parameters ΔR on the reliability of the force field. The study of that dependence is important to derive geometries of excited states and to foresee relative intensities in the SERS spectrum starting with quantum chemically computed geometries [4]. In this work we discuss the effects of perturbations of the force field on the ΔQ shifts obtained from ab initio computed geometries. The obtained results are analyzed to predict the SERS spectrum of pyridine enhanced by a charge transfer process (SERS-CT) [5]. In that particular case, the theoretical spectrum would allow to decide whether that resonant mechanism is present or not. The relevance of this lies on the circumstance that in SERS-CT processes the excited state is almost unknown given that it is identified as the radical anion.

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P14.2

CONCERNING COMPUTATIONS IN VIBRATIONAL SPECTROSCOPY

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Molecular spectroscopy, and in particular it's vibrational part, is a creature of the XX-th century, this jubilar XXV-th EUCMOS being the last one in that, and the millennium. Thereby is sensible have a glance backwards, and to give a tribute those who were among the founders and first recognized contributors. It is impossible even to count all of them, but we ought to name at least Nobel prize winner in chemistry (1971) Gerhard Herzberg, and as inventors of normal coordinate analysis - E.B.Wilson and M.A.Elyashevich.

The Laboratory of Molecular Spectroscopy at Moscow State University was founded more than 50 years ago by V.M.Tatevskii. As concerned modern computations in vibrational spectroscopy - the main problem, which attracted a special attention during last decades, was the so-called inverse problem, i.e. force field determination (the direct problem, i.e. calculations of vibrational frequencies and normal modes, being considered as a trivial one). There are different approaches toward solving inverse problems, belonging to the ill-posed problems. We used new stable numerical methods for that first in the framework of purely empirical approach. After rapid progress in quantum mechanical calculations of harmonic force fields for moderate size molecules at different (HF, MP2, DFT) levels some new fundamental possibilities became available for more accurate interpretation of experimental data and improving methods of empirical force fields calculations.

On this base the concept of regularized quantum mechanical force field (RQMFF) was introduced, and a new formulations of inverse problems were given. This new approach was illustrated with concrete numerical applications. It should be emphasized, that by all means only some kind of effective force field can be received with harmonic approximation. The main goal of such efforts is accumulation of some effective values of force constants, transferable within large set of related compounds. The best criterion of tranferability would be a coincidence of experimental and calculated vibrational frequencies within experimental measuring errors. Hereby is advertising of our book on the subject:
A.G.Yagola, I.V.Kochikov, G.M.Kuramshina and Yu.A.Pentin, "*Inverse Problems of Vibrational Spectroscopy*", VSP, Utrecht, The Netherlands, 1999, 297 p.

FROM STRETCHING FREQUENCIES TO BOND ENERGIES: A NEW APPROACH

P14.3

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The straight line relations between the stabilization energies of hydrocarbon radicals, $E_s(R^\bullet)$, and the stretching frequencies of the bonds R-H, RO-H, R-OH and N-H in MeCONHR are shown to exist. The $E_s(R^\bullet)$ values are defined by the equation $E_s(R^\bullet) = D(CH_3\text{-}H) - D(R\text{-}H)$, where D is the bond dissociation energy, To find the corresponding correlation equations the reliable D values are needed. The D(R-H) data published and recommended in different reviews were used and compared and corresponding correlation equations of the type $E_s(R^\bullet) = f(\nu)$ were obtained for stretching frequencies of the bonds listed above. It is worth to note that the $E_s(R^\bullet) = f[\nu(C\text{-}H)]$ correlation dependencies for saturated and unsaturated hydrocarbons are dissimilar. The IR spectra of complex biologically active compounds (menadione and retinol) and of a conjugated alcohol (3-methylpent-2-ene-4-yn-1-ol) in solutions were recorded. The found ν(C-H) and ν(C-O) frequencies were used to calculate the $E_s(R^\bullet)$ values of corresponding radicals and D(R-H) values of parent hydrocarbon molecules. The possibility of predicting the R-H bond strengths for different hydrocarbons from the known stretching frequencies using the derived correlation equations was discussed. The D(R-H) values of different C-H bonds (primary, secondary and tertiary) were calculated and recommended bond strengths are tabulated and compared with the published ones. The approach was also applied to the IR spectra of peroxy radicals. The published C-OO$^\bullet$ stretching frequencies of methyl, ethyl, i-propyl, *t*-butyl and allyl peroxyls were discussed and the IR spectrum of allyl peroxyl was reinterpreted. The plot of $E_s(R^\bullet)$ values of the radicals against the $\nu(C\text{-}OO^\bullet)$ frequencies is a straight line with correlation coefficient $r = 0.997$. The dependency may be used to predict the unknown $\nu(C\text{-}OO^\bullet)$ values of peroxy radicals.

P14.4

OBTAINING SCALED QUANTUM MECHANICAL FORCE FIELD FOR BIG SIZE MOLECULES

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Recently, we have implemented a method [1] to obtain automatically a quantum mechanical scaled Force Field within the procedure of Pulay [2]. The method is based on the so-called trivial force constant matrix [1]. In the present work, the performance of the method is checked by taking relatively big size molecules: anthracene and naphthalene, as example tests. The obtained results agree quite well with those published by other authors [3].

Additionally, the fitting of the calculated to observed vibrational frequencies has been improved by using an alternative technique [4], which basically consists in the refinement of the previously scaled Force Fields. The key step in this procedure is the generation of an intermediate matrix, $C\Lambda C^T$. Such a refinement amounts only a small correction to the scaled force constants, yielding a considerable improvement of the fitted frequencies. This scheme of refinement can be applied to any kind of reference system used in the definition of the internal coordinates.

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TRANSFERABILITY OF PULAY'S SCALE FACTORS IN THE IVa GROUP OF THE MENDELEYEV PERIODIC SYSTEM

P14.5

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Ab initio quantum mechanical calculations were performed for structures and force fields (HF/6-31G*//HF/6-31G*,[1])) of 3,3-dimethylbutene-1, cyclopropene, 1-methylcyclopropene, and 1-trimethylsilyl-, 1,2-bis(trimethylsilyl)-, 1-trimethylgermyl-, 1,2-bis(trimethylgermyl)-, 1-trimethylstannyl-, and 1,2-bis(trimethylstannyl)-3,3-dimethylcyclopropene. The Pulay's scale factors [2-5] for correction of the quantum mechanical force fields of cyclopropene, 1-methylcyclopropene, and 3,3-dimethylbutene-1 were determined using the experimental vibrational frequencies of only light isotopomers of these molecules. The set of scale factors obtained was transferred to the quantum mechanical force fields of all the other molecules mentioned above. The vibrational problems for these molecules were solved. Complete vibrational analyses were carried out for the whole set of these related compounds. Transferability of scale factors for series of related compounds of cyclopropene with heteroatoms from the IVa column of the Mendeleyev Periodic System of chemical elements was demonstrated.

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P14.6

CANONICAL FORCE FIELD OF XY_3 (D_{3h}) MOLECULES: BF_3 AS AN EXAMPLE

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The use of the simple valence internal coordinates (SVIC's) for the description of the molecular potentials has been a disccused topic from the begining of the development of the theoretical basis for the analysis of the molecular vibrational spectra. Clearly, the force constants expressed in term of SVIC's, i.e. bond stretchings, angle bendings, torsions, etc, have a deep physicochemical meaning. However, from long time it was understood that individual and unambiguous values of them could not be obtained for molecular systems where redundant relations were present.

In the eigthies, Kuczera [1,2], proposed a way for the obtention of the above mentioned individual values. Later, during the ninethies our group was working on the application of the Kuczera's ideas in XYn branched molecules [3]. Recently, we have been able to give a complete treatment of this problem [4] which firmly supports the previous works on this subject.

We think the series of the boron halures constitutes a very favourable and chemically interesting choice for the exploration of one of the properties of the canonical molecular potentials in terms of SVIC's, i.e. the transferibility of force constants among similar molecules. The pure trihalures, XY_3, show D_{3h} point symmetry and their mixed trihalures derivatives, XY2Z, XYZW present C_{2v} and C_s point symmetries, respectively; thus, in the present work we propose to extend the canonical treatment in the force fields of this series of molecules and to investigate the afore mentioned transference capability. Concretely, for this meeting we present our initial results for the BF_3 molecule.

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RULE KNOWLEDGEBASE FOR PREDICTION OF MOLECULAR FRAGMENTS FROM ^{13}C NMR SPECTRA

P14.7

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The recognition of chemical structures, which is realized by spectroscopic methods, is very important in many research fields. Irrespective of the applied spectral methods, the basic step in structure elucidation is the interpretation of the spectrum. This process demands professional education, experience, and very often also intuition. For the interpretation of spectra, the chemist uses mainly semiempirical methods, which are based on large amounts of previously accumulated reference data (spectra libraries, and tables of spectrum-structure correlations). As searching through large collections of data, as well as selecting and applying various empirical rules by conventional means, is generally very time-consuming and quite often rather boring, many approaches to the computer-aided (e.g. semiempirical) interpretation of spectral data have been proposed. Three main structure elucidation techniques may be distinguished: the library search method, the pattern recognition method, and the rulebase generation method.

Various papers dealing with the matter of computer-aided structure elucidation have been published. However, these systems are being continuously developed and improved. [1-3]. The paper describes the program that searches a given ^{13}C NMR spectral database for spectral features characteristic for selected molecular fragments. These spectrum-structure correlations condensed into a set of interpretation rules (a rule knowledgebase) are applied to the interpretation of an unknown compound spectrum in order to predict whether the respective molecular fragments are present or absent in the unknown molecule. As the source of spectral-structure data, two databases were used. One of them comprises 2500 ^{13}C NMR spectra of chemical compounds. The other comprises the information about the structural formula of compounds, i.e. molecular graphs [4]. As the training set, 1500 spectra were selected by an algorithm which generated spectra randomly. The remaining spectra formed the test set. The program is currently being implemented on a PC microcomputer (CELERON 466MHz DTK, HDD 13,5GB, FDD 1.44MB, CD-ROM 44X, VGA Matrox Millennium G400 16MB).

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P14.8

HIERARCHICAL NEURAL NETWORK MODELLING FOR IR-SPECTRA RECOGNITION

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The purpose of this research was to demonstrate a new approach to multilevel hierarchical modelling using artificial neural networks (ANN). In a situation where the data set is small and error-prone it is necessary to build multiple models of input-output relationships, combining these models into a hierarchical structure. There are several techniques for combining of ANN outputs, varying from the simple averaging [1] to the weighted averaging [2] using different methods of weights calculation. Nevertheless, all these techniques use some linear combination of outputs. We propose a non-linear combining of results of the non-linear predictors, where the outputs of low-level predictors serve as the inputs of higher-level predictor. For the low-level (first) of modelling we used feedforward ANN with resilient propagation learning algorithm [3] for supervised learning on the training set. The goal of modelling was to build relationships between IR-spectra under study, and the vectors of their responses. Two different ANN models (with shortcut connections and full-connected) were built at the first step. The performance of trained nets was tested on the test set, which contained patterns not included in the training set. For the higher-level (second) of modelling we needed a network that allowed us to extract the dependencies between input data, i.e. the network that is able to solve a subtype of a general problem of spatial pattern memorising. Thus we have selected an example of simultaneous recurrent networks (SRN), which uses multiple iterations (not just one feedforward pass) in order to represent the association between input and output data [4]. At this level, the results of prediction made by both networks of previous level were used as the inputs of SRN.

The suggested method was applied to the interpretation of spectra of modified starches (56 starches of different origins - corn, potato, and rice). This has definite practical value, since authentication of food is very important for the consumers and the food industry at each level of the food chain from raw materials to finished products. The results of this study demonstrated more powerful ability of the new approach than a conventional selection of the best model or than linear combining of outputs.

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ESTIMATION OF PROTEIN SECONDARY STRUCTURE FROM FTIR SPECTRA USING NEURAL NETWORKS

P14.9

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Different spectroscopic approaches, such as FTIR, CD and Raman spectroscopy can be used for the characterisation of protein secondary structure. Although qualitative information on secondary structure can be easily obtained using these techniques, quantitative analysis is not straightforward. For example, several different approaches are used for estimation of protein secondary structure from FTIR spectra of proteins. These include curve fitting, partial least squares analysis, and factor analysis techniques. All of these methods have varying degrees of advantages and disadvantages. Here we explored a different approach based on neural networks. The most important problem in designing a neural network (NN) is the following generalization: a NN is expected to make good predictions when data not present in the training set is used as an input. If the size of the training data set is not sufficiently large for a given NN complexity or if the NN is overtrained by forcing the error to very small values, then the trained NN may not have the ability to generalise. In our study we had FTIR spectra for 18 water-soluble proteins, recorded in water. The secondary structure contents of these proteins are known from X-ray crystallography. Due to the small size of the available data set leave-one-out method has been used. 17 of the spectra are used for training and the remaining spectrum is used for testing. In addition, 101 data samples are available over the 1700-1600 cm^{-1} region of each spectrum. However, a NN with 101 inputs, having a few hidden neurons, will require a data set much larger than 17 spectra. Therefore, the first step is to reduce the number of input connections by employing an efficient data reduction method on the FTIR spectra. We used Discrete Cosine Transform which is known to compact the energy in a very low number of transform coefficients for highly correlated data.

Results of our preliminary studies will be presented and the advantages and disadvantages of the NN approach, in comparison to other existing methods, will be discussed.

P14.10

CORRELATION BETWEEN STRUCTURAL, OPTICAL AND RAMAN ENHANCING PROPERTIES OF SILVER FILMS

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For spectroscopical applications the study of mechanisms of surface enhanced Raman scattering (SERS) by statistical methods (with use of integral parameters) is actual with the purpose to build-up the phenomenological SERS theory.

In the present work by using the methods of a mathematical statistics (correlation, regression and factor analysis) the correlation of optical and Raman enhancing properties of silver films (SF) with parameters of their surface was studied and the equations of a nonlinear regression were obtained, and also the factors of enhancement by various types of SF of Raman scattering by pyrene were calculated.

It is established, that optical parameter most influencing effectiveness of an electromagnetic enhancement of pyrene Raman scattering, is the ratio of a maximal optical density to a half-width of an optical density band of SF D_{max} / ($\Delta\lambda/2$). Thus the increase of values of both this parameter and SERS intensity happens as a result of structurally-dependent resonant increase of a local surface electromagnetic field of silver clusters (islands) in the case of comparable sizes of islands and distances between them.

The empirical dependences between parameter D_{max} / ($\Delta\lambda/2$) and SERS intensity of pyrene can be represented by exponential curves: Y=C+exp (b0+b1*X).

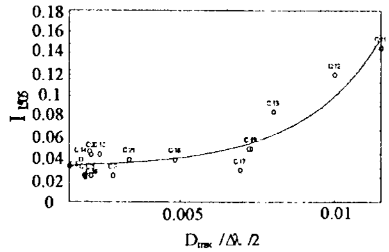

Fig. 1. Exponential regression curve obtained as a result of a nonlinear estimation of dependence of intensity of the pyrene SERS band at 1505 cm^{-1} (I_{1505}) from parameter D_{max} / ($\Delta\lambda/2$)

To increase SERS intensity from molecules similar to pyrene (when the enhancement depends, generally, on the electromagnetic mechanisms, but not on specificity of adsorption) it is recommended to apply the SF with high values of parameter D_{max} / ($\Delta\lambda/2$) (more, than 0,01) and with difference between wavelength in a maxima of an optical density and wavelength of excitation no more, than 50nm.

The minimal value of enhancement factors of pyrene Raman scattering both by as-deposited, and annealed silver films are insignificant (about 10^4), that testifies to low concentration of active sites for pyrene molecules.

Acknowledgements:The work was supported by Grant INTAS 97-0522 and the Ministry of Education of Belarus.

EFFECTIVE BOND CHARGES FROM INFRARED INTENSITIES IN CH_4, SiH_4, GeH_4 and SnH_4

P14.11

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The effective bond charges method (EBC) [1,2] was applied in interpreting the infrared intensities of the ν_3 and ν_4 bands in CH_4, SiH_4, GeH_4 and SnH_4. The experimental intensity data used are from the works of Hiller and Straley [3] for CH_4 and of Coats, McKean and Steele [4] for SiH_4, GeH_4 and SnH_4. The experimental effective bond charges are compared with *ab initio* estimates obtained at different levels of theory. The effective X-H bond charges (X=C, Si, Ge, Sn) characterize polar properties of these bonds. The EBC values are rationalized in terms of static and dynamic charge contributions accompanying vibrational distortions.

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P14.12

ELECTRODYNAMICS OF DYE-SOLVENT MIXTURE

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In the study the description of electromagnetic field dynamics in photoactive molecular material in the frame of the conception of extended phenomenological electrodynamics is considered. For the description of the material structure, the phenomenological concept of multicomponent body is applied. In such an approach it is supposed that the body consists of the perfectly and uniformly mixed components (solvent-dye molecules) and all components of the body are allowed to be present at each place of space simultaneously. It seems that molecular system as a mixture of dye molecules and solvent perfectly fulfil above phenomenological assumption of multicomponent body. In such a system dynamics of electromagnetic field is expressed in the Lagrange-Hamilton formalism. The concept of phenomenological extended electrodynamics is based on the physical hypothesis that electric charge and magnetic spin momentum are independent and immanent attribute of the matter. The continuum of the neutrons of the average life-time of order of 1000s which is sufficient long for electrodynamic phenomena, is a good example occurring in nature and can support our supposition.

In mathematical model the state of field is represented by two independent vector field functions [1,2]. These functions and their derivatives are the set of the independent Langrange variables. Such an approach allows to introduce the Lagrange-Hamilton equations of the field and lets to omit the difficulties of the classical electrodynamics. From the mathematical point of view the physical field is a function which is dependent on time and space co-ordinates. The notion, particle and time, is interpreted as primary ideas with accordance to the continuum physics. By a particle of multicomponent body (solvent molecules and dye molecules) we understand the system which occupies the space. The physical variables are continuous in this space and the space occupied by the set of body particles is treated as a geometrical point. The space occupied by all components simultaneously is interpreted as a point of continuum. For physical system (solvent- dye molecules) understood in such a way, the conception of extended phenomenological electrodynamics is applied.

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THE METHOD FOR CALCULATION OF OPTICAL AND DIELECTRIC PARAMETERS FROM LIMITED SPECTRAL DATA BASED ON MODIFIED FORM OF KRAMERS-KRONIG RELATION

P14.13

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The real and imaginary parts of complex refractive index or complex dielectric constant are connected to each other by the Principle of Casuality which is formulated mathematically by the Kramers-Kronig dispersion relations. The direct application of these relations requires the knowledge of spectral data in infinite frequency range. In practice, we deal with data in a limited spectral range, and one need to use some approach to extend the spectra in a plausible way. A considerable success in this direction was achieved in works of Jones and co-workers, Bertie et al., Zelsmann, and many others. In our approach, we have promoted the ideas developed by Ahrienkel and by Roessler, and rewrite the Kramers-Kronig relation in a modified form, allowing to exploit the reference points (minimum of 3 points are required) with more efficiency. The method proposed is applicable for data obtined from both transmittance and reflectance measurements.

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Computational Methods in Spectroscopy

-Diatomics & Weakly Bound Systems
-Simple Organic Molecules
-H-Bonded Systems

INTERACTION DIPOLE MOMENT OF THE WEAKLY BOUND COMPLEXES OF CARBON DIOXIDE WITH RARE GASES.

P15.1

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We report a self-consistent field (SCF) and Møller-Plesset Perturbation Theory (MP) study of the electric dipole moment of the weakly bound complexes of CO_2 with He, Ne, Ar, Kr and Xe. We rely on carefully optimized, large basis sets of Gaussian-type functions. We have investigated the basis set dependence of the interaction dipole moment at the equilibrium configuration. Dipole moment curves have been obtained for specific geometric configurations of the $CO_2 \cdots X$ complexes.

P15.2

AB INITIO ROVIBRATIONAL SPECTROSCOPY OF HYDROGEN SULPHIDE

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Potential energy hypersurfaces (PES) and a dipole moment surface (DMS) have been constructed for the ground electronic state of H_2S by state-of-the-art *ab initio* quantum chemical techniques, most notably by higher-order coupled cluster (CC) theory and basis sets ranging from [S/H] [6*s*5*p*3*d*2*f*/4*s*3*p*2*d*] to [8*s*7*p*5*d*4*f*3*g*2*h*/6*s*5*p*4*d*3*f*2*g*]. Small corrections, including basis set extrapolation to the complete basis set (CBS) limit, scaling to the full configuration interaction (FCI) limit, relativistic terms, core polarisation and core correlation effects, as well as the diagonal Born–Oppenheimer term (DBOC) have been investigated and incorporated into the final PES. Using the exact kinetic energy operator and the discrete variable representation (DVR) approach, rovibrational energy levels and their intensities have been computed utilising the different *ab initio* PESs and the DMS. The final fully *ab initio* PES of this concerted study reproduces the experimentally available vibrational band origins (VBOs), up to 15 000 cm^{-1}, of several isotopomers with an accuracy of 1–10 cm^{-1}. Prediction of the rotational lines, up to $J = 17$, is better than 2 cm^{-1}. These results allow thorough investigation of many issues related to determination of PESs and DMSs, *e.g.*, the effect of relativistic vs. DBOC terms on VBOs. Relevant spectroscopic issues concerning H_2S, including vibrational adiabaticity and anharmonic resonances, local-mode behaviour of vibrational terms, the density of vibrational states, the signatures of quantum ergodicity, and the four-fold clustering effect of the rotational lines have also been studied.

THE INFRARED SPECTRA OF WEAK MOLECULAR COMPLEXES

P15.3

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The structures, interaction energies and vibrational spectra of a number of weak molecular complexes have been determined by means of a series of *ab initio* calculations, at the MP2 level of theory and using the 6-311+g(d) basis set. The range of complexes includes those with either carbon monoxide or nitrogen as electron donor and either carbon dioxide, nitrous oxide, carbonyl sulphide or carbon disulphide as electron acceptor. In the case of the carbon monoxide adducts, both C-bound and O-bound structures have been studied. The relative stabilities of the complexes have been compared, and rationalized on the basis of the physical properties of the elctron acceptors.

The predicted infrared spectra (wavenumbers and intensities) have been used to determine the wavenumber shifts on complexation, and the complex/monomer intensity ratios. These have been correlated with the computed energies of interaction, corrected for basis set superposition error. The wavenumber shifts have been employed in comparing the computed spectra with those obtained by co-condensing the interacting monomer species in cryogenic matrices, and will be used in the interpretation of new spectra of the presently unknown complexes.

P15.4

VIBRATIONAL ANALYSIS OF NICOTINIC ACID SPECIES BASED ON *AB-INITIO* MOLECULAR ORBITAL CALCULATIONS

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Many articles have been published on pyridine carboxilic acids concerning their vibrational spectra [1], SERS effect [2] and as ligands in several coordination compounds with biological properties [3]. Vibrational assignments based on *ab-initio* calculations [4] and normal coordinate analysis [5] have been reported for methyl-pyridines, but for pyridine carboxilic acids such calculations have not been performed yet.

The experimental Raman frequencies of the nicotinic acid species in aqueous solution were obtained, and in order to get the vibrational assignment, an *ab-initio* calculation of the optimized structure and frequencies of the main equilibrium species of nicotinic acid was done.

The optimized structure and vibrational band frequencies of the three species derived from nicotinic acid were calculated at the Hartree-Fock (HF) and at the second-order Møller-Plesset perturbation level (MP2) and by Becke's three-parameter hybrid Density Functional Theory method using the Lee-Yang-Parr correlation functional (B3LYP). The 6-31G** basis set was used throughout. All the calculations were carried out using the Gaussian 94 and Gaussian 98 programs on IBM/SP2 9076 at NPD-UFSC and DEC-ALPHA 4100 at LCCA-USP.

The main results obtained from the calculations are:
i) the three main species are planar, with C_s symmetry;
ii) a good agreement between the calculated in-plane frequencies and the experimental ones was observed, even considering the molecule in the vacuum. The HF calculated scaled frequencies showed a better fitting than the other two methods, specially for the modes involving COO^- vibrations;
iii) there is a considerable mixing of the ring modes and also mixing of some ring modes with substituent vibrations, for instance the symmetric ring breathing (ν_1) and the ring deformation (6a) modes are mixed with $\delta(COO^-)$;
iv) the ring β(CH) deformation modes in the 1100-1400 cm^{-1} region are the most difficult to be assigned because of the great number of close frequencies and also because of the mixing of these modes with C-X stretching and substituent vibrations.

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P15.5

THEORETICAL CALCULATIONS OF THE TICT ELECTRONIC STATE AND β-VALUE FOR SOME DI-PHENYL POLYENES P,P'- AND O,O'- DI-SUBSTITUTED

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The semiempirical method AM1-MOPAC/93(1) was employed to optimize the geometry and to calculate the molecular second-order hyperpolarizability, β-value, of all conjugated molecules type p,p' and o,o' D-Phenyl-(CH=CH)n-Phenyl-A, (D,A-DPH), where D and A are the electron-donating and -accepting groups of $-(NCH_3)_2$, $-OCH_3$ and CN, NO_2. The semiempirical method HAM/3-CI(2) was used to calculate excitation energies including the experimentally observed(3,4) "twisted intramolecular charge transfer" (TICT) excited state. The spectroscopic properties of TICTstate in D,A,-DPH are very sensitive to the donor and acceptor substituents and also to the solvent polarity(3,4). Constituted here were two series of polymers: series (A) with p,p'-substituents: (1) $[N(CH_3)_2]$, (NO_2); (2) (OCH_3), (OCH_3); (3) $[N(CH_3)_2]$, (CN); (4) (NO_2), (NO_2); (5) (CN), (CN); (6) (OCH_3), (CN); (7) $[N(CH_3)_2]$, $[N(CH_3)_2]$; (8) (CN),(NO_2), (9) (OCH_3), $[N(CH_3)_2]$ and (10) (OCH_3),(NO_2) and series (B) o,o'-substituent: (1) $[N(CH_3)_2]$, (NO_2); (2) (OCH_3), (OCH_3); (3) (OCH_3), $[N(CH_3)_2]$ and (4) (CN),(CN).The results of HAM/3-CI calculations indicate that all molecules with twisted conformation produce an increase at the dipole moment and all molecules where D and A are groups of restricted internal rotation (e.g. $-N(CH_3)_2$ and $-NO_2$ as much p,p'as o,o') has the lowest singlet state (S_1) (n,π^*) assigned as TICT state involving a transition from the n orbital of D to the π^* orbital of A group. For example, the polymer A1 with n=2,3,4, shows a TICT state with following energies: 2.03eV; 1.82eV; 1.54eV respectively. On the other hand, the polymer A2, where D and A are groups of free internal rotation (e.g. OCH_3) with n=2,3,4, we didn't assign the (S_1) state calculate as TICT state . The β-values calculated increase in polymer as A1 with n=2,3,4, the values are: $=55\times10^{-30}$esu, 48x $\times10^{-30}$esu e 38 $\times10^{-30}$ esu, respectively, compared with DPH, the values are: $=0{,}032\times10^{-30}$esu, $0{,}006\times10^{-30}$esu e $0{,}104\times10^{-30}$esu, respectively. Both semiempirical methods are useful tool to study these aspects of optical nonlinearity in p,p'and o,o', D,A,-DPH systems.

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P15.6

AN AB INITIO AND DENSITY FUNCTIONAL STUDY OF THE POTENTIAL ENERGY SURFACE AND VIBRATIONAL SPECTRUM FOR THE FORMIC ACID

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In the present work, the dimeric structures located on the potential energy surface (PES) for formic acid were investigated using HF, MP2, B3LYP and BLYP theoretical approaches.

Vibrational analysis is a strong tool to study the distinct dimeric structures of carboxylic acids. By using theoretical methods, we can assess how the vibrational modes are modified by the formation of the hydrogen bonds.

The PES for formic acid presented several distinct dimeric structures, being stabilized by O...O and O...C hydrogen bonds (Fig.1). The most stable forms are represented in Fig.1 with the association energies (ΔE^{ass} in kcal/mol) found to be –18.13 (a) and –11.42 (b) (MP2/6-31G** values). At the B3LYP/6-31G** and HF/6-31G** levels, the calculated ΔE^{ass} were: -19.64 (a), -11.67 (b) and –15.21 (a), -9.81 kcal mol^{-1} (b) respectively. The frequencies and the vibrational intensities obtained in all levels of calculation, were fitted to a Lorentziana type function for the description of the infrared spectra. In the Fig.1 we have the theoretical infrared spectra for the two most stable dimers of formic acid, where the assignments of the main vibrational modes are presents.

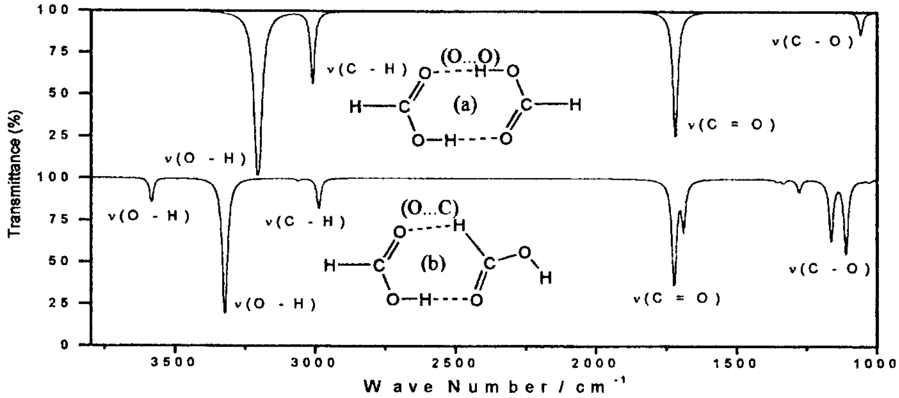

Fig.1 – Theoretical vibrational spectra and structures of the two most stable dimers of formic acid.

As shown in fig.1 despite the formation of the hydrogen bonds the spectra are found to be distinct, showing great differences between the vibrational modes of specific functional groups.

Using this analysis we can identify characteristic absorption of distinct structures, which coexist in solution, helping experimentalists to elucidate some ambiguous points of the experiment.

P15.7

PREDICTION OF THE VIBRATIONAL SPECTRA AND MOLECULAR STRUCTURES OF TETRA-ALKYLHYDRAZINES USING SECOND GENERATION MOLECULAR MECHANICS FORCE FIELDS. RELEVANCE TO ELECTRON TRANSFER REACTIVITY.

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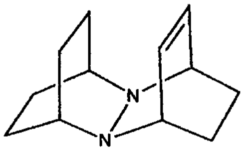
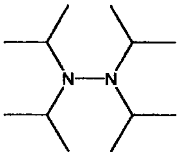
The kinetics of electron transfer reactions of tetraalkylhydrazines has received some attention in the past [1,2]. It has been suggested that, for these molecules, the conformation around the N-N bond plays a very important role in their reactivity and in the kinetic mechanism of electron transfer reactions. Therefore, the knowledge of the structural parameters of the N-N moiety, in particular, the N-N distance and the prefered torsion angles around this bond, is essential to fully understand the different electron transfer reaction rates shown by different members of this family of compounds.

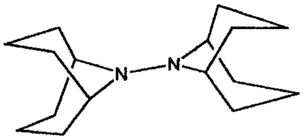
In this work, three tetraalkylhydrazines with pseudo first order rate constants covering a wide range of values were considered:



A. 22/u22



B. iPr$_2$N)$_2$



C. 33N)2

Despite x-ray diffraction studies of the crystalline forms of **B.** and **C.** were already reported [3], it was clear that more systematic anc complete structural and vibrational information on these compounds was still required in order to enable the establishment of a reliable relationship between their structure and reactivity.

Hence, in this work, the conformational spaces of the three sellected molecules were studied by Molecular Mechanics, using a second generation force field, and the vibrational spectra of the relevant conformers were calculated. The results could be successfully correlated with the available x-ray diffraction data and give further support to the explanations previously made concerning the importance of the geometry of the N-N moiety to the hydrazines rate constants for electron transfer [1].

The Infrared and Raman spectra of the three molecules were also obtained experimentally and assigned taking into consideration the results of the theoretical predictions. Special emphasis was given to the N-N stretching mode, since its frequency is related with the average barrier-crossing frequencies activated at the transition state for electron transfer [1].

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P15.8

AN *AB INITIO* STUDY OF THE STRUCTURAL AND VIBRATIONAL PROPERTIES OF THE C_3H_6-HCN, C_2H_4-HCN AND C_2H_2-HCN HYDROGEN COMPLEXES

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In this work, we present a comparative study of the structural and vibrational properties of the C_2H_2-HCN, C_2H_4-HCN and C_3H_6-HCN hydrogen complexes. It is well established that the ground vibrational state molecular structures of these complexes are T-shaped near-prolate asymmetric rotors. Here the molecular geometries of these complexes and of their isolated molecules were fully optimized at the MP2/6-311++G** level of calculation using the GAUSSIAN 92 Program on a IBM RISC 6000 computer.

The more pronounced effects on the structural parameters of the isolated molecules due to complexation are verified to the CC and HC bond lengths which are directly involved in the H-bond formation. They are increased after complexation. The calculated H-bond lengths calculated from the carbon atom of HCN to the midpoint of the CC bond are in very good agreement with the experimental ones, i.e, 3.668 Å (3.656 Å), 3.721 Å (3.711 Å) and 3.482 Å(3.476 Å) in C_2H_2-HCN, C_2H_4-HCN and C_3H_6-HCN, respectively. The experimental values are given in parenthesis.

As expected, the more pronounced effect on the normal modes of the isolated molecules after complexation occurs to the H-CN stretching mode. The H-C stretching frequency is shifted downward whereas its IR intensity is much enhanced upon H-bond formation. This increase on the H-C stretching intensity is due to the charge-flux term, which is strongly affected by complexation, in contrast to what happens with the hydrogen charge. On the other hand, the vibrational frequencies and the IR intensities of the proton acceptor molecules are little affected by complexation.

The MP2/6-311++G** intermolecular stretching frequencies are in good agreement with the available experimental values, analogously to what was found for the acetylene-HX and HCN-HX complexes using this same level of calculation [1-3]. Here the values found were: 90 cm^{-1} (82 cm^{-1}), 83 cm^{-1} (75 cm^{-1}) and 87 cm^{-1} (80 cm^{-1}) for the C_2H_2-HCN, C_2H_4-HCN and C_3H_6-HCN complexes, respectively. Finally, the other new vibrational modes arising from complexation show several interesting features.

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VIBRATIONAL SPECTRA AND DFT CALCULATIONS OF SALICYLIDENEANILINE AND BENZYLIDENEANILINE

P15.9

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Salicylideneaniline (SAN) is an interesting example of photochomic and thermochromic transformations. Structural differences of SAN tautomers can be understood from their vibrational spectra.

Vibrational dynamics of SAN is interesting to be compared with that of trans-benzylideneaniline (tBA). Optimized geometries and vibrational modes were calculated by the DFT method with the B3-LYP functional and 6-31G* basis set. Calculated force constants were scaled using the recent scaling factors by Pulay et al. Infrared intensities and potential energy distribution were also calculated. The same procedure was applied to the tBA molecule.

The results show a very good agreement with experimental spectra, which enable a full assignement of IR and Raman spectra of SAN and tBA. The results of both DFT calculations and experimental spectra for two related molecules and their isotopomers will be compared and discussed.

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P15.10

ELECTRIC MULTIPOLE MOMENTS FOR SO_2, SEO_2, TEO_2 AND THE OPEN AND CLOSED FORMS OF S_3, SE_3 AND TE_3.

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The electric dipole, quadrupole, octopole and hexadecapole moment of SO_2, SeO_2, TeO_2 and the open and closed forms of S_3, Se_3 and Te_3 have been obtained from Self-Consistent Field (SCF), Møller-Plesset Perturbation Theory (MP) and Density Functional Theory (DFT) calculations. Systematic trends have been investigated in the series O_3, SO_2, SeO_2, TeO_2 and the series O_3, S_3, Se_3 and Te_3 (both C_{2v} and D_{3h} symmetries).

STRUCTURE AND STABILITY OF OCNNCO AND SCNNCS ISOMERS

P15.11

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Pseudohalide ions, such as cyanate (OCN), fulminate (CNO), and thiocyanate (SCN), are well know for a long time and they have a wide and varied chemistry. They are bidentate, thus they form two series of molecules containing the pseudohalide group, the so called 'normal' and 'iso' derivative. Very little is known, however, about the parent pseudohalogens. Table 1 shows the pseudohalogens, which can be derived from the cyanate and fulminate group, as well as from their thio analogues.

The aim of this work is to characterize all possible pseudohalogens and to obtain information about their thermodynamic and kinetic stability, using theoretical ab initio and DFT methods. Of particular interests are the structure, stability, and isomerisation mechanisms. Generation, IR and fotoelectron spectroscopy of the most stable isomers are also discussed.

	-N=C=X	-X-C≡N	-C≡N=X	$\text{-X-}\overset{+}{\text{N}}\equiv\overset{-}{\text{C}}$
X=C=N-	XCN-NCX			
N≡C-X-	NCX-NCX	NCX-XCN		
X=N≡C-	XNC-NCX	XNC-XCN	XNC-CNX	
$^{-}\text{C}\overset{+}{\equiv}\text{N-X-}$	CNX-NCX	CNX-XCN	CNX-CNX	CNX-XNC

Table 1 – Pseudohalogens investigated (X= O, S)

P15.12

VIBRATIONAL SPECTRA OF 4-FLUORANILINE: A SCALED FORCE FIELD

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It is well-known that the ab initio calculations overestimate the harmonic vibrational frequencies with respect to the fundamentals observed experimentally. This is due to different reasons such as the use of finite basis sets, the incomplete incorporation of the electronic correlation and the neglect of anharmonicity effects in the theoretical treatment. However, the calculated ab initio frequencies can be fitted to the experimental ones by following the scaled quantum mechanical force field (SQMFF) methodology [1,2]. It has been demonstrated that this method allows one not only to obtain a good overall agreement between the theoretical and experimental frequencies but also to identify the corresponding fundamental frequencies in molecules with a large number of atoms [3,4].

The force field of 4-Fluoraniline has been calculated at the RHF/6-31+G* level of theory. It has been shown that this level of calculation is adequate to reproduce the non-planarity of this molecule in the ground electronic state [5]. The vibrational spectrum has been calculated from the scaled force field. The same scale factor is used within each type of internal coordinates. Afterward, the calculated spectrum is compared with the Raman spectrum measured by us, and with the infrared spectrum, taken from the literature [6] and an assignment of the fundamental modes have been made. Furthermore, due to the success of density functional density theory (DFT) in predicting chemical and physical molecular properties we have also calculated the force field at the B3LYP/6-31+G* level and it is compared with the SQM force field. The assignment of 4-Fluoraniline is compared with that of the aniline [7] in order to determine the substitution effect of the hydrogen atom for the fluorine atom.

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DENSITY FUNCTIONAL STUDY ON VIBRATIONAL SPECTRA OF 1,2,5-OXADIAZOLE AMINODERIVATIVES (AMINOFURAZANS).

P15.13

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The previous calculations [1,2] have shown that the DFT(B3LYP) method predicts both geometrical parameters and vibrational modes of 1,2,5-oxadiazole (furazan) with high accuracy. However the prior studies on vibrational spectra for 1,2,5-oxadiazole aminoderivatives (possessing a number of biological activities) are very limited [3,4]; we could not find any analysis of these spectra using theoretical methods.

Here, we exploit density functional theory in analysing the vibrational spectra of four aminofurazans, namely, 3,4-diaminofurazan, 3-amino-4-methylfurazan, 3-amino-4-nitrofurazan, and 3-amino-4-cyanofurazan (Figure 1). We present DFT calculations for equilibrium geometries, vibrational frequencies and absolute infrared intensities for individual vibration modes, using the B3LYP density functional and 6-31G (d,p) basis set via GAUSSIAN 94/DFT software. These results are compared with available experimental data. The influence of substituents on geometrical parameters and fundamentals of furazan cycle is also discussed.

DFT(B3LYP) calculated cycle bond length and angles in aminofurazans are close to corresponding experimental data. DFT overestimates exocyclic C-NH_2 bond, but reproduces exocyclic distances C-CH_3 in (II) and C-NO_2 in (III) very well. The calculated (unscaled) frequencies of furazan cycle vibrations for aminofurazans are in good agreement with the experiment (average errors of 19, 23, 18 cm^{-1} for I, II, IV, respectively); and these modes are not particularly sensitive to the nature of the substituent. The calculated NH_2 stretching vibrations are in poorer agreement with the experiment, but DFT(B3LYP) predicts the NH_2 bending vibrations of useful accuracy.

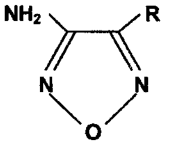

Figure 1. R = NH_2 (I), R = CH_3 (II), R = NO_2 (III), and R = CN (IV).

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P15.14

THE O-H(D) STRETCHING POTENTIALS OF THE HYDROGEN BONDED WATER MOLECULES IN $MCl_2{\cdot}2H_2O$ ($M\in$\{Mn, Co, Fe\}). *AB INITIO* AND DENSITY FUNCTIONAL STUDY

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The uncoupled *anharmonic* O-H(D) stretching vibrations of the hydrogen bonded water molecules with local C_2 symmetry in compounds of the type $MCl_2{\cdot}2H_2O$ (where $M\in$\{Mn, Co, Fe\}) were studied at various levels of theory, within the finite-cluster approach. The studied clusters consisted of one water molecule coordinated to the metal atom and hydrogen bonded to two chloride anions. The vibrational potential energy curves for the uncoupled OH stretching vibrations were obtained from pointwise energy calcultions at HF and DFT levels of theory. The H atoms were allowed to vibrate against the rigid OD fragments (all other structural parameters of the cluster were held fixed at the experimental values). The obtained energies were least-squares fitted to a fifth order polynomial in $\Delta r = r_{OH} - r_{OH,e}$ ($r_{OH,e}$ being the equilibrium values), and the one-dimensional vibrational Schrödinger equation was solved variationally, diagonalizing the vibrational Hamiltonian within the harmonic oscillator basis.

For the pointwise energy calculations, both the standard HF SCF and gradient corrected density functional methodologies were employed. Within the DFT approaches, Becke's three-parameter hybrid exchange functional was applied in combination with the Lee-Yang-Parr (B3-LYP), Perdew-Wang 91 (B3-PW91) and Perdew 86 (B3-P86) correlation functionals. To solve the HF or the Kohn-Sham equations, the standard triple-zeta quality 6-311G(d,p) basis set was used on O, H and Cl, while the transition metal atoms were treated within the LANL2DZ basis, employing an effective core potential (ECP) description of the inner shell electrons.

From the calculated energies of the vibrational eigenstates, both the fundamental *anharmonic* and harmonic vibrational frequencies, as well as the anharmonicity constants were computed. Theoretical values were compared to the experimental ones, as well as to those computed by various approximate approaches. The influence of the electron correlation effects upon the calculated quantities is discussed.

STRUCTURE AND SPECTRA OF $(H_20)_{11}$ and $(H_2O)_{12}$ WATER CLUSTERS BY AB INITIO CALCULATIONS

P15.15

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The present study belongs to a series of our investigations of $(H_20)_n$ structures and spectra in the three-dimensional size regime *n*. Size selected OH spectra of the pertinent clusters have been recently measured and interpreted with the help of calculations [1-3]. Now, the optimal structures, interaction energies and OH stretching and bending frequencies of water cage clusters $(H_20)_{11}$ and $(H_20)_{12}$ have been investigated by *ab initio* calculations. The proposed lowest energy structures are derived employing an empirical polarizable potential, as in our previous papers [1,2]. The final study consisted of MP2 level *ab initio* calculations of optimal structures and IR spectra. The main structural units in these clusters are three-coordinated molecules of two varieties: double donor-single acceptor (DDA) and single donor-double acceptor (AAD). In term of these units the structures of the clusters is discussed.

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P15.16

THEORETICAL VIBRATIONAL SPECTRA OF DIKETENE MOLECULE, ITS ISOMERS AND THEIR SULPHUR ANALOGUES

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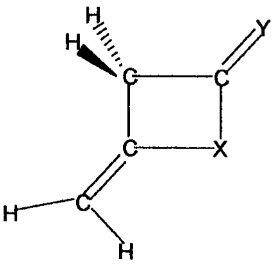
Diketene molecule, its 2- and 3-methylene isomers and their sulphur analogues (1, 2 and 3 respectively), where X, Y stand for O, S atoms, are desired products of catalytic synthesis.



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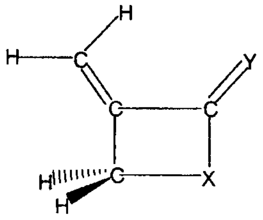

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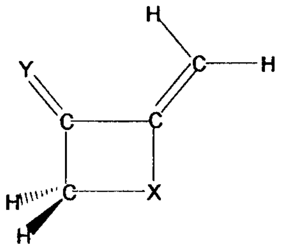

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So far, only diketene (1; X=Y=O) and 3-methylene-2-oxetanone (2; X=Y=O) derivatives have been obtained experimentally. In our previous studies we examined the theoretical IR and Raman spectra of diketene molecule and its 3-methylene isomer [1] and studied the energetics and theoretical NMR spectra of the whole set of diketene isomers and sulphur analogues [2]. In the present paper we analyse selected vibrational modes which can be used to distinguish particular compound and serve the qualitative analysis of reaction mixtures. The studies on energetics [2] allow us to judge which compounds can be formed due to the reaction of $CH_2=C=Y$ with allene molecule or the reaction of $CH_2=C=X$ with $CH_2=C=Y$ molecule.

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P15.17

THEORETICAL IR, RAMAN AND NMR SPECTRA OF 1,2- AND 1,3-DIMETHYLENECYCLOBUTANE

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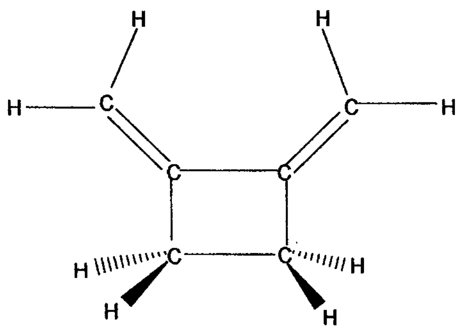
Equlibrium geometries, rotational constants, harmonic vibrational frequencies, infrared intensities, ^{1}H and ^{13}C NMR spectra have been calculated for 1,2-dimethylenecyclobutane and its less stable isomer 1,3-dimethylenecyclobutane (1 and 2 respectively) using MP2, DFT (B3PW91) and RHF theoretical methods with 6-311++G** basis set.



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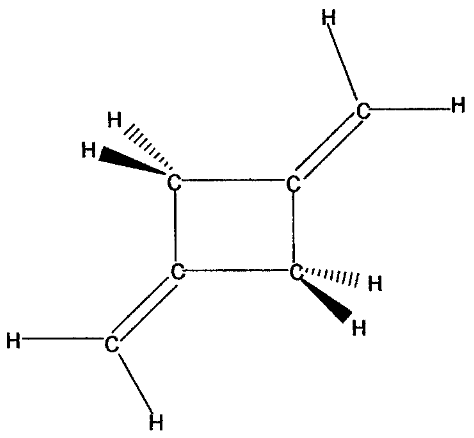

2

Mixture of these compounds was obtained in the dimerization reaction of two allene molecules [1]. Nowadays, several less stable isomers can be obtained by irradiation of 1,2-dimethylenecyclobutane in rare-gas matrixes [2].

Studied properties calculated theoretically have been compared with experimental values, if available. The internal coordinates were defined for both isomers and used in potential energy distribution (PED) analysis. The theoretical vibrational and NMR spectra form the basis to differentiate particular compounds in the reaction mixture.

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P15.18

THE EQUILIBRIUM STRUCTURE, HARMONIC FORCE FIELD AND FREQUENCIES OF PYRIDINE – AB INITIO AND DFT STUDIES

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The equilibrium structure, harmonic force field and frequencies of pyridine have been computed by the second-order Møller-Plesset, MP2, and coupled cluster, CCSD(T), approaches. The one-particle basis sets were the correlation-consistent polarized basis sets, cc-pVnZ. In this way, the high-level benchmark data were obtained. These results were compared with results of the calculations by various density functional (DFT) methods. The performance of the pure and hybrid functionals is discussed.

MOLECULAR MODELLING AND SPECTRAL STUDY OF SOME 1 N-R1-3N-R2-1,3,4-TRIAZOLIUM METHYLIDE

P15.19

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Some new carbanion mono- and di- substituted 1-N-R1-3-N-R2-1,3,4-triazolium methylides, recently sinthesized have been subjected to a molecular modelling based on library CAChe programs[1,2]. The studies were achieved by multiconformational analysis (MM2 with improved parameters and AM1 methods. NMR, IR and UV VIS spectra were used to study the stability and reactivity of these compounds. The molecular electric dipole moments were theoretically and experimentally estimated.

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P15.20

NMR SPIN-SPIN COUPLING CONSTANTS IN WATER MOLECULE. EQUILIBRIUM AND ROVIBRATIONAL VALUES.

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Equilibrium ${}^1J_{OH}$ and ${}^2J_{HH}$ coupling constants and their respective rovibrational contributions have been calculated for water at the CAS (complete active space) and RAS (restricted active space) MCSCF (multiconfigurational self-consistent field) level using large basis sets.

An additive model [1] that takes into account the effect on the coupling constants of excitation of more than two electrons and of core electron correlation is used to estimate the coupling constants. The best calculated ${}^1J^{TO}_{OH}$ and ${}^2J^{TO}_{HH}$ values, some of them including the rovibrational contributions, are presented in Table 1 together with the Fermi contact (J^{FC}) and the non-contact (J^{NC}) contributions. These values agree satisfactorily with the experimental ones [2] and with those recently calculated [3] at the SOPPA (CCSD) level.

The not negligible correlation effect on ${}^1J_{OH}$ associated to the core electrons is compared with those calculated for ${}^1J_{XH}$ in HF, NH_3 and CH_4. These effects seem to be proportional to the heavy atom electronegativity. On the contrary, the core correlation effect on the geminal coupling is small. The rovibrational contributions were calculated from a spin-spin coupling surface fitted up to quartic order using the ab initio force field developed at the CCSD(T) level by Császár et al [5].

Table 1. Experimental and calculated ${}^1J_{OH}$ and ${}^2J_{HH}$ couplings (in Hz).

Method	${}^1J^{FC}_{OH}$	${}^1J^{NC}_{OH}$	${}^1J^{TO}_{OH}$	${}^2J^{FC}_{HH}$	${}^2J^{NC}_{HH}$	${}^2J^{TO}_{HH}$	Ref.
EOM-CCSD	-65.45	-9.45	-74.90	-11.12	0.30	-10.81	[4]
SOPPA(CCSD)	-69.09	-12.46	-81.56	-11.87	3.29	-8.58	[3]
SOPPA(CCSD)[a]			-77.22			-8.03	[3]
(CAS/RAS)SCF[b]	-69.26	-12.10	-81.36	-11.52	2.97	-8.55	This work
(CAS/RAS)SCF[a]			-76.78			-7.88	This work
Exp			-80.6(1)			-7.11(3)	[2]

[a] Vibrationally averaged results.

[b] $J^{FC}(R54(0\rightarrow2)) + [J^{FC}(R24(0\rightarrow4)) - J^{FC}(R24(0\rightarrow2))] + [J^{FC,full}(R49(0\rightarrow2)) - J^{FC}(R49(0\rightarrow2))]$, and $J^{NC}(R23(0\rightarrow2)) + [J^{NC}(C13) - J^{NC}(R13(0\rightarrow2))]$.

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COMPUTATIONAL STUDIES OF THE ^{1}H AND ^{13}C NMR ISOTROPIC CHEMICAL SHIFTS USING DENSITY FUNCTIONAL OPTIMIZED GEOMETRIES. II. SACCHARINE AND THIOSACCHARINE

P15.21

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A combined quantum chemical and experimental study of the ^{1}H and ^{13}C isotropic chemical shift values in saccharine and thiosaccharine was performed. The geometries of the studied species and of the tetramethylsilane (TMS) were optimized at gradient-corrected density functional level of theory, with Berny's optimization algorithm (calculating the energy derivatives with respect to nuclear coordinates analytically). Becke's exchange functional was used in combination with the Lee-Yang –Parr correlation one (B-LYP). The standard double-zeta qualtiy 6-31G(d,p) basis set was used for orbital expansion to solve the Kohn-Sham equations. The ^{1}H and ^{13}C NMR shielding tensors for the BLYP/6-31G(d,p) optimized geometries were calculated using three approaches for achievement of gauge independence: Gauge Independent Atomic Orbitals (GIAO), Continuous Set of Gauge Transformations (CSGT) and the Individual Gauge for Atoms in Molecules (IGAIM).These calculations were performed at various theoretical levels, both with and without an inclusion of the dynamical electron correlation effects, using a TZ+P quality 6-311G(d,p) basis set for orbital expansion. Both standard Hartree-Fock (HF/6-311G(d,p)), as well as BLYP/6-311G(d,p) and B3LYP/6-311G(d,p) levels of theory were employed.

The isotropic shielding values were used to calculate the isotropic chemical shifts with respect to TMS. Both the chemical shift values (with respect to TMS) and the relative shielding values (with respect to the most deshielded center within the molecule), computed at HF and DFT levels of theory, were compared to the experimental data. The assignment of ^{1}H and ^{13}C NMR spectra were performed by different homo- and heteronuclear one- and twodimensional NMR techniques (^{1}H-^{1}H and ^{1}H-^{13}C COSY, NOESY, *etc.*). We found that calculated quantities correlate well with the experimental ^{1}H and ^{13}C NMR chemical shifts, regardless of the level of theory.

The performances of the employed methods for achievement of gauge invariance as well as the inadequacy of the description of paramagnetic contribution to the shielding tensor within the Kohn-Sham approach is discussed. The importance of explicit inclusion of the dynamic electron correlation effects in calculations of the chemical shift values in the case of particular centers within the studied systems is elaborated.

P15.22

THEORETICAL STUDY OF THE STRUCTURE AND VIBRATIONAL SPECTRA OF $VO_2X_2^-$ (X= F, Cl, Br, I)

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Molecular geometries for anions of general formula $VO_2X_2^-$ (X= F, Cl, Br, I) have been investigated theoretically at different Hartree-Fock and post-Hartree-Fock levels of theory using different basis sets. Calculations were performed at Restricted Hartree-Fock (RHF) with Lanl2DZ , 3-21G, 6-31G* and 6-311+G* basis sets, Moller-Plesset second order perturbation theory (MP2) with lanl2DZ basis set and, finally, Density Functional Theory (DFT) with Becke's three parameter functional with correlation for exchange in conjunction with Lee, Yang and Parr's non-local correction to correlation, i.e. B3LYP, with Lanl2DZ, 3-21G, 6-31G* and 6-311+ G* basis sets They all were carried out by means of Gaussian98 package (1).

From an experimental point of view, the only structural data at disposal to be used for comparison were those for the chloro derivative, $VO_2Cl_2^-$, coming from a X-Ray diffraction study (2).

In order to assess the nature of the stationary point reached for molecular geometry optimization and to check which level of theory best reproduces the experimental data, we also made calculations of vibrational frequencies at the same levels of theory and basis sets as pointed before. The results for $VO_2Cl_2^-$ and $VO_2F_2^-$were compared with a previous experimental report (3) and, as a conclusion, we obtained that RHF/Lanl2DZ results were those best behaviour observed.

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INVESTIGATIONS OF THE STRUCTURE OF POLYMORPHOUS MODIFICATIONS OF FLUOROALKYLCYCLOHEXANECARBOXYLIC ACIDS BY INFRARED SPECTROSCOPY METHODS

P15.23

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The new results of investigations of polymorphism and mesomorphic states of fluorinated derivatives of alkylcyclohexanecarboxylic acids (nFACHCA, n=4, 7, where n is the number of carbon atoms in the fluoroalkyl radicals) have been discussed. The methods of vibrational spectroscopy (experimental, theoretical modelling) have been used. The samples have been investigated in the 100-500 K temperature range, the spectra have been recorded in the range of 33–4000 cm^{-1} [1-3]. The frequencies of normal modes and intensities of bonds of IR spectra have been calculated by fragments method [4] for conformers of H-complexes with various orientations of fluoroalkyl radical and carboxylic group relative to the rest part of the molecular complex. The influence of H-bonds on dynamic of H-complex, polymorphic crystalline modification and mesophase formation were determined. The polymorphism of nFACHCA is conformational. The transitions solid crystal - liquid crystal - isotropic liquid and solution are accompanied by H-bonds system reconstruction: the dimers, open associates, chain associates with different energy of hydrogen bound and monomers have been appeared.

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P15.24

INFRARED SPECTRA AND NORMAL COORDINATE ANALYSIS OF QUINOLINE AND QUINOLINE COMPLEXES

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Normal coordinate calculations were used to predict the vibrational spectrum of quinoline. Quinoline was taken as planar and semiempirical quantum optimised geometry (MNDO) has been calculated by using GAMESS [1] program. For the theoretical calculations of the IR spectral properties, program LEV [2] was used. The initial force field parameters of quinoline were refined from the corresponding parameters of benzene and pyridine molecules. After refinement procedure the difference between experimental and theoretical wavenumbers was found to be less than ± 10 cm^{-1} for most of the vibrations. The results for the force field parameters, the vibrational modes in internal coordinates, the displacement of the atoms from their equilibrium positions and potential energy distribution are presented. A partially common and well transferable force field has been obtained for the free quinoline and in the first step, this force field was introduced in calculating the IR spectra of the transition metal(II) quinoline complexes. Later the force field was refined in order to obtain the experimental IR spectra of the quinoline complexes. The calculated spectra have been compared with the experimental spectra of quinoline halide complexes. They showed good agreement. The results indicate that the geometry and the bond properties of the quinoline do not change substantially upon coordination. The frequencies of the phenyl and pyridine rings in different complexes are rather similar except the lower wavenumbers.

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HYDROGEN BONDED NETWORKS OF METHOXY SUBSTITUTED α-PHENYLCINNAMIC ACIDS STUDIED BY SPECTROSCOPIC AND COMPUTATIONAL METHODS

P15.25

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Recently, the aggregation behaviour of the methoxy derivatives of α-phenylcinnamic acid methyl esters have been studied by spectroscopic and computational means [1]. It was found that in solution the esters do not form molecular assemblies, while in the crystalline state hydrogen bonding interactions arise. Two hydrogen bond types could be detected, both involving the oxygen of the methoxy substituent. They were of $(CH_3)O...H-C$(aromatic) or, occasionally, $(CH_3)O...H-C$(olefinic). In the work leading to this contribution similar types of interactions were searched for, but between methoxy substituted α-phenylcinnamic acid molecules. Beside identifying $(CH_3)O...H-C$(aromatic) hydrogen bonds, we expected to detect $(CH_3)O...H-C$(olefinic) hydrogen bonds that we failed to see when the agglomeration of α-phenylcinnamic acids were studied [2].

The compounds of this contribution were the *E*- and *Z* isomers of 2-phenyl-3-(2'-methoxy-phenyl)-propenoic acid, 2-(2'-methoxyphenyl)-3-phenylpropenoic acid and 2,3-bis(2'methoxy-phenyl)-propenoic acid. IR spectroscopy was the primary experimental tool for identifying hydrogen bonding interactions. Samples in solution as well as in crystalline form were measured and spectra were compared. As an auxiliary ^{13}C NMR spectroscopy was also used for investigating structure forming features in both sample types. Based on measurements networks of various types were constructed and possible hydrogen bonding was studied by computational means too (the PM3 semiempirical quantum chemical method, full geometry optimization).

Experimental and computational methods revealed that short range arrangement through mainly dimerization existed in solution, while extended hydrogen bonding networks were typical in the crystalline state. In these networks the methoxy substituent played crucial role, since it was the extra hydrogen bonding site, which established the connection between the dimers. The interaction was $(CH_3)O...H-C$(aromatic) hydrogen bond. The position of the proton of the aromatic ring in hydrogen bonding (relative to the site where the other part of the molecule is attached) was determined through molecular modeling. It was either para or meta, but never ortho, due to steric reasons. Neither experimental nor computational evidence for $(CH_3)O...H-C$(olefinic) hydrogen bond could be found. Its formation seems to be restricted, possibly due to steric reasons, once again.

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P15.26

CHARGE TRANSFER IN HYDROGEN BOND COMPLEXES

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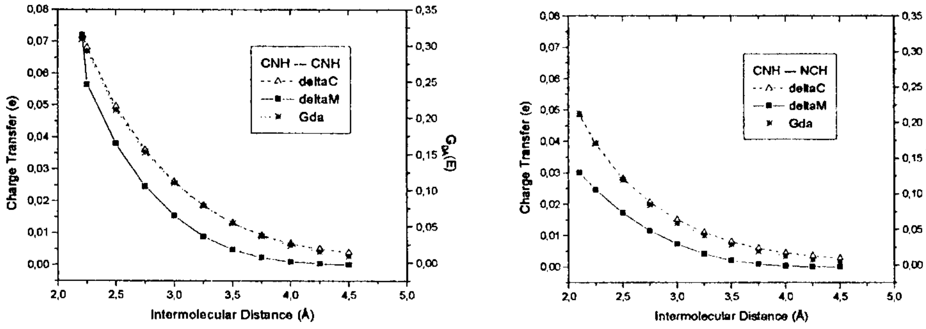
Ab initio RHF/4-31G** calculations were performed in order to investigate the charge transfer process in H-bonded systems and to establish a correlation between the atomic polar tensor (APT) elements and the effective interaction factor calculated from the off-diagonal elements of Green's function ($G_{da}(E)$).

The variation of Mulliken and Corrected charges between the isolated monomer and the monomer into the complex were calculated for the CNH-CNH and CNH-NCH hydrogen complexes. The Corrected charges were obtained from the charge-flux charge-overlap-modified (CCFOm) model, derived from the infrared intensities. The effective interaction factor $G_{da}(E)$ was calculated from the atomic orbitals centered at the donor and acceptor molecules using the Green's function formalism and it quantifies the electron donor/acceptor character of the interacting molecules. The dependence of the charge transfer and $G_{da}(E)$ with the intermolecular distance was obtained and are represented in Figure 1.



(a)

(b)

Figure 1. Dependence of the charge transfer and $G_{da}(E)$ with the distance for (a) CNH-CNH and (b) CNH-NCH systems. deltaC = charge variation from APT analysis, deltaM = charge variation from Mulliken analysis and $G_{da}(E)$ = effective interaction factor.

From Figure 1 it can be seen that the charge transfer and $G_{da}(E)$ have an exponential dependence with the donor-acceptor distance. It should also be noted that the behaviour of the Corrected charges with the distance is very similar to that of the $G_{da}(E)$, in contrast to the Mulliken charges.

These are important results since they establish a quantitative relationship between the APT elements and the Green's function elements, where the latter ones have been applied to the electron transfer in biologic systems model, for instance.

Spectroscopy and Chemical Analysis

DIFFERENTIATION OF MOTOR USED OILS ON THE BASIS Of THEIR IR SPECTRA. PART I. APPLICATION OF THE CORRELATION METHOD

P16.1

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One of the most commonly investigated materials for criminalistic purposes in the cases of road accidents is motor oil. The oil traces are revealed on clothing of victims as greasy stains, arising as a result of contact of the victim with the chassis of a vehicle. In the course of a criminalistic examination an oil sample extracted from the fabric is compared with oil taken from the suspected car in order to establish their similarity to each other.

The chemical analysis of oil microsamples is preferably performed by means of FTIR method. It requires a small amount of a sample, which can be prepared for analysis in relatively simple way. Moreover, it provides rich information on the sample composition in terms of both the hydrocarbon base and different kinds of additives improving the quality of oils.

It has been already stated that the FTIR method is able to differentiate the samples of various brands of fresh oils [1,2], as well as the samples of a given oil taken for analysis in some initial time range of its exploitation [3,4]. However, the infrared spectra of oils become more and more similar to each other if the samples of an oil or even different oils are successively examined after long time of using them by the same car or by different cars [3]. So, a risk arises, being great from the criminalistic point of view, that among the suspected cars the wrong one can be indicated as guilty if the expertise is based exclusively on the FTIR results.

The aim of the investigations presented was to find a simple mathematical method being sensitive enough to differentiate the chemical composition of an oil used to a large extent on the basis of its infrared spectra. As the initial attempt made was to apply the method of Pearson's correlation coefficient. The spectra of progressively used oils of two brands (Castrol GTX and ELF Sporti Super) were compared with these corresponding to fresh oils of the same brands. The changes were observed in various ranges of wavelengths and estimated in relation to the random fluctuations of the signals measured. It has been proved that the FTIR method is capable of providing information detailed enough if some specific fragments of spectra are examined by means of the correlation method.

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P16.2

SPECTROSCOPY FOR ANALYSING A SOLID WASTE

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Incineration allows the management of Municipal Solid Waste (MSW), thereby reducing landfilling demands and simultaneously recovering energy. In Portugal, these processes are starting now in two plants (Valorsul – near Lisbon, and Lipor – in the area of Porto).

A disadvantage of incineration is the production of a waste when the MSW burns, named fly ash, which is the particulate matter carried over from the combustion chamber and removed from the flue gas stream. In this work, fly ash residues, which is considered as an hazardous waste due to its chemical composition (heavy metal and large amount of soluble salts, will be characterised.

The chemical matrix of MSW incinerator residues is very complex and the measurement of the individual elements can be difficult. For chemical characterisation, destructive methods or non-destructive analytical techniques can be used. In our work Flame Atomic Absorption Spectroscopy (FAAS) has been used to measure transition and alkaline elements in the referred hazardous waste. Since FAAS is a destructive method, the fly ashes are firstly extracted with leachate fluids (such as water or acid solutions), and filtered through a 0.45m filter before being analysed through this technique. The elements analysed are Pb, Cd, Cr, Ni, Cu, Zn, K and Na, and the results show that the toxicity of the fly ash residues from MSW incineration is mainly associated to lead (Pb) concentration on the eluate. These results are in agreement with the ones mentioned in similar studies [1,2].

When the FAAS technique is used there are two areas of concern: the choice of flame conditions on a per element basis (in our study air/acetylene) and the high concentration of salts (since the viscosity can be increased and cause problems with aspiration of the sample into the flame). In the analysis performed in a Perkin-Elmer equipment, it has been possible to obtain reliable results without technical problems.

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IR-SPECTROSCOPIC EXAMINATION OF DEFECTS IN CONSTRUCTION POLYMER MATERIALS

P16.3

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The durability of construction polymer materials (CPM) to a great extent depends on the character and value of intermolecular interactions (II) between chains in polymer block. The less regular intermolecular net is the more defects fields are in it. There are internal tensions in defects fields that leads to CPM destruction at last.

IR-spectroscopy is a very useful method for examination of intermolecular net because polymers have IR-bands sensitive to II and to conformation regulation (CR) of polymer chains. IR-examination of II and CR at different temperatures gives opportunity to come to conclusions about intermolecular net regulation in polymers and defects of polymer materials. The more regular net is, the narrower temperature interval is necessary for changing of II and CR.

Chains segments with weak II are destroyed at lower temperatures than it is necessary for segments with strong II. Therefore temperature examination of IR-bands sensitive to II and CR could give a true notion of CR and polymer material defects.

We elaborated the vacuum cell with Multiple Attenuated Reflection (MATR) accessory which gives an opportunity to examine polymer materials at temperatures from -160° up to +300° C. The character of intermolecular net was investigated in CPM on the base of polyethylene terephthalate and polybutylene terephthalate and also in network polystyrenes.

P16.4

CORRELATION BETWEEN SPECTROSCOPIC ELLIPSOMETRY AND TAUC AND CODY MODELS FOR POROUS SILICON OPTICAL BANDGAP EVALUATION

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The room temperature visible photoluminescence of porous silicon (PS) leads to the assumption that it is behaving like a wide band gap material, which present direct interband transitions[1]. Consequently, questions about the value of the optical bandgap are arising in order to identify the light emission mechanism.

In our work the spectroscopic ellipsometry (SE) characterization technique in correlation with Cody [2] and Tauc [3] models was used to determine the optical bandgap E_g of PS. The results are compared with E_g obtained by Wemple DiDomenico model for the same samples and reported in other work.

The SE is a proper technique for obtaining optical properties of thin solid films, particularly for PS layers. The PS films were simulated by Effective Medium Approximation [4] (Bruggeman model) considering a multilayer structure of different crystalline silicon (c-Si), amorphous silicon (a-Si) and voids mixtures. The simulated spectra were compared with the experimental spectra and the best fit was chosen. Using the best simulation, the refractive index (n) and the absorption index (k) were calculated in 1.5-4.0 eV spectral range. Measurements were done on PS obtained electrochemically on p^+ silicon substrate.

Cody and Tauc have proposed each one a model for estimating the optical bandgap of amorphous materials. Taking into account that PS can be considered a non-crystalline material, it is possible to evaluate by Tauc and Cody models the value of optical bandgap. Cody model gives a very simple relation for k of a non-crystalline semiconductor as a function of E_g and photon energy ($\hbar\omega$):

$$k^{\frac{1}{2}}(1/\hbar\omega) = A - B(1/\hbar\omega)$$

The Tauc model gives also a very simple relation for E_g evaluation.

From the SE measurements were obtained the k values versus ($\hbar\omega$). From the linear fit of $\sqrt{k}$ versus ($\hbar\omega$) or versus ($1/\hbar\omega$), considering the Tauc and Cody models, were obtained and discussed the E_g values.

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SURFACE ANALYSIS OF ORGANIC THIN LAYERS

P16.5

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The application of organic thin layers becomes more and more important in Philips products (e.g. coatings, plastic electronics etc.). Knowledge of the chemical composition of the outer monolayers is therefore of great importance. The CFT Materials Analysis department offers help in gaining insight into the composition and structure of these layers, including solving problems in manufacturing processes. Surface analysis plays a key role in the materials programs of Research and Development. Adequate characterization is indispensable to obtain the desired functional properties of the thin layers. Therefore, a number of complementary techniques as e.g. Auger, FT-IR, SEM, SSIMS and XPS are a requisite.

By means of round robin tests of model- and real live samples the strengths and weaknesses of FT-IR, SSIMS and XPS will be ranked. By cooperation and good knowledge of the strengths of the techniques we will improve our analytical support for the analysis of organic thin layers.

P16.6

SPECTROSCOPIC STUDY (SERS, DRIFT AND NMR) OF DIFFERENT HUMIC SUBSTANCES

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The chemical analysis of complex mixtures such as soil humic acid (HA) represents a serious analytical problem when the main objective is to study the structure or conformation of these macromolecules in aqueous solution. These macromolecules dissolved or dispersed in aqueous solution can show size distribution and spontaneous changes in their conformational and aggregation states in relation to the environmental conditions (pH, ionic strength, and presence of di- or multivalent metal ions) (1,2).

In this work the results of a spectroscopic study (SERS, DRIFT and NMR) on the HA structure and conformation extracted from peat, lignite and leonardite samples are reported. The HAs of each sample showed a different content in main functional groups such as carboxylate, hydroxyl, ether, aliphatic, aromatic, polycondensed aromatic moieties. In particular, the pH effect influenced significantly the conformation of these macromolecules in aqueous solution.

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MOLECULAR INVESTIGATION OF THE AGING OF ASPHALTENE MOLECULES IN PETROLEUM

P16.7

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A problem often encountered during petroleum production and transport is the precipitation of high molecular weight components: asphaltenes and waxes. The waxes are generally paraffins with an average carbon number of nearly 42. Asphaltenes are high molecular weight aromatic compounds, surrounded and linked by aliphatic chains and heteroatoms. The phenomenon of spontaneous precipitation of high molecular weight components, particularly asphaltenes, has been investigated by analysis of the precipitates of an unstable oil for a period of two weeks after its extraction from the pipeline. These precipitates have been filtered; on the filtered oil the asphaltenes still in solution have been precipitated by adding n-heptane and compared to the insoluble ones. The precipitates both spontaneous and by n-heptane addition were treated in soxhlet with n-heptane at nearly 100°C to dissolve the waxes which were analyzed by Gas-Chromatography. The remaining asphaltenes have been characterized molecularly by FT-IR, ^{1}H and ^{13}C-NMR, GPC and structurally by XRD. These analyses show a clear evolution of molecular features of asphaltenes with time which can be described as an aging of the heavier aromatic compounds in the oil. In particular, at longer times the asphaltene molecules tend to be less aromatic but more polar.

The flocculation of asphaltenes, which causes their spontaneous precipitation, has been followed with SAXS (Small Angle X-Ray Scattering) directly in crude oil by analyzing small amounts of oil always taken from the same position in the test tube at different days. After an initial lowering of aggregates concentration, which is expected considering the spontaneous precipitation, the SAXS data show an subsequent increase at longer time.

This new phenomenon combined with the evolution of molecular characteristics of asphaltenes suggests that during aging of the oil new aromatic molecules (the "resins") become unstable owing to their tendency to aggregate in the oil.

P16.8

SPECTROSCOPIC STUDIES OF MOLECULAR AGGREGATION OF ASPHALTENES

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Asphaltenes are one of the primary components of crude oils and have been the subject of a variety of studies in order to obtain more information about their tendency to form molecular aggregates adsorbed onto solid surface and precipitate. These properties are responsible of some problems in oils industry processes such oil extraction and transportation.

In this work we present the results of a spectroscopic study of asphaltenes from Venezuelan crude oils. The techniques used are based on Laser Spectroscopy: Fluorescence, Time Resolved Fluorescence, Z-scan technique and molecular absorption.

In the absorption spectra of asphaltenes in Toluene, a red shift is observed as the concentration increase. This shift in the absorption band have been reported in the case of aggregate formation where the strong coupling of several self, similar monomer results.

The fluorescence spectra were obtained by sample excitation with 488 and 514,5 nm CW Ar laser beam. In the emission spectra no shift is observed, this results have been reported by others authors using others crude oils, this phenomenon is not due transference charge between structures, so is a consequence of collisional effect. The studies of asphaltenes varying the solution concentration shows a change in the curve slope, this results are related with the critical micellar concentration; similar results were obtained with time resolved Fluorescence Spectroscopy of asphaltenes.

The evidences of asphaltenes aggregation were also observed through the application of Z-scan technique to study the nonlinear optical response of solution of asphaltenes in Toluene. Strong dependence of the two photon absorption coefficient (β) with the input intensity was observed for concentration. The results suggest that a change in (β) and its saturation behaviour occur a consequence of aggregation.

Analysis of results suggest that asphaltenes form aggregates with the increase of concentration solution, typical of micelle formation.

STRUCTURAL INVESTIGATION AS A FUNCTION OF COMPOSITION OF THE $NaCl-Na_2B_4O_7-Na_3AlF_6-TiO_2$ SYSTEM

P16.9

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The quaternary system: $NaCl-Na_2B_4O_7-Na_3AlF_6-TiO_2$ was proved to be a promising electrolyte for the electrosynthesis of high purity TiB_2 powders with controlled granulometry. However the mechanism of the TiB_2 obtaining is far for being elucidated because of the inadequate structural information.

X-ray diffraction, Ir, UV-Vis and (MAS and High Temperature) NMR spectroscopy were employed in order to establish the structural evolution of the above mentioned system

Structural changes of the tenary mixtures: $Na_2B_4O_7-[Na_3AlF_6-TiO_2]_x$ (where $x \leq 11$ wt. % TiO_2) and the $NaCl-Na_2B_4O_7-Na_3AlF_6-TiO_2$ quaternary mixtures were determined in accordance with the electrolysis requirements, i.e. optimum B/Ti atomic ratio (e.g. B/Ti=12-20), adequate viscosity of the electrolyte and energy consumption. Moreover, it is known that electroactive species $[BF_4]$ and $[TiF_6]$ are very important for TiB_2 yielding as thin film in the oxofluoro electrolites, at the beginning of the electrolysis.

Thus, in the present study on the $NaCl-Na_2B_4O_7-Na_3AlF_6-TiO_2$ melts, criolite dissociation, as complex anions: $AlF_y^{(y-3)-}$ (y=6, 5 and 4) and F^-, can cause conversion of the borate groups into oxofluoro complexes of the boron: $B(O, F)_4$ and of $[TiO_4]$ into hexacoordinated titanium species: $[TiF_6]$ and $[TiF_5O]$, for a B/Ti atomic ratio less than 20. This behaviuor is the result of competition between similar sized anions, O^{2-} and F^-, for high field-strength cation neighbours.

P16.10

TEMPERATURE DEPENDENT FT-IR SPECTROSCOPIC INVESTIGATION OF ADSORPTION OF 3- AMINOPYRIDINE ON SEPIOLITE AND MONTMORILLONITE FROM ANATOLIA

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Sepiolite is composed of trimorphic layers arranged in chains (ribbons) which are joined through oxygen ions. It is composed of continuous and two-dimensional tetrahedral layers with T_2O_5 (T= Si, Al,..) composition and discontinuous octahedral layers. Octahedral layer discontinuity leads the formation of internal channels in the structure, which provides high absorptive capacity. Montmorillonite is an expanding layer silicate mineral, composed of aluminosilicate layers stacked one above the other. Each layer has small net negative charge because of isomorphous substitution of ions in the framework. The charge is compensated by interlayer hydrated cations, which are known as exchangeable cations. It is well known that montmorillonite can accommodate various types of compounds in its interlayer space to give an intercalation type of inclusion compounds.

In this study, the adsorption of 3-aminopyridine by natural sepiolite and montmorillonite from Eskisehir (Anatolia) was investigated in the temperature range from 20 to 150^{0}C by infrared spectrometry using a variable temperature unit. The spectroscopic results indicate that the 3-aminopyridine molecules adsorbed on sepiolite are coordinated to Lewis acidic sites and/or surface hydroxyls by H-bonding interaction through pyridine ring nitrogen lone pairs. Moreover amino group hydrogens are found to be involved in hydrogen bonding interaction with water molecules ($NH \cdots OH_2$). Surface Bronsted acid strength of sepiolite is weak and 3-aminopyridinium is not detected under the conditions applied in this study. It must be noted that the adsorption of aminopyridine affected the hydroxyl group vibrations of sepiolite. The intercalation of 3-aminopyridine within montmorillonite has been shown by x-ray diffraction to increase the interlayer spacing. IR spectroscopy indicates that sorbed 3- aminopyridine by montmorillonite are mostly coordinated to exchangeable cations directly or indirectly through water bridges.

FT-IR SPECTROSCOPIC INVESTIGATIONS OF BENZIDINE AND BIPYRIDYLS ADSORBED ON DIATOMITE FROM ANATOLIA

P16.11

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Diatomite is a siliceous rock made up largely from the skeletons of aquatic plants called diatoms. Apart from being made of fossil skeletons diatomite is essentially opaline hydrous silica. It is used as an absorber of hazardous chemicals in handling and storage and refining various acids [1]. Oxidative properties of clays and some metal oxides have been widely studied during recent years using simple organic molecules which are sorbed and then react at the surface yielding colored products. Diatomite has been known to be colored with N,N-dimethylaniline [2]; accordingly, it seemed interesting to study the adsorption and interaction characteristics of some aromatic molecules with diatomite by using IR spectrometry. In this study we have investigated FT-IR spectra of benzidine, 2,2'-bipyridyl and 4-4'-bipyridyl adsorbed on natural diatomite from Kutahya-Alayunt (Anatolia).

FT-IR spectra of benzidine (bnz), 2,2'-bipyridyl (2,2'-bpy) and 4-4'-bipyridyl (4,4'-bpy) adsorbed samples indicate the presence of chemisorbed species. No physical sorbed species have been detected. Bnz and 2,2'-bpy treated diatomite samples were found to be colored whereas 4,4'-bpy treated diatomite was not altered in color. In the case of sorbed bnz, formation of radical cationic (bnz^+) surface species has also been detected to a relatively small extend. We also propose that generation of the 2,2'-bpy anion takes place via electron transfer process from the surface to the organic molecule, in the case of 2,2'-bpy treated diatomite. However spectroscopic results indicates that the concentration of the negatif species must be comparatively very low. Effects of the thermal treatment on diatomite-organic molecule complexes have also been investigated.

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P16.12

QUANTITATIVE DETERMINATION OF EPOXIDIZED SOYBEAN OIL USING NEAR INFRARED SPECTROSCOPY AND MULTIVARIATE CALIBRATION

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Vegetable soybean oil is often used in the industry as addictive for PVC films. When epoxydized it confers stabilized features to the films by that inhibiting thermal degradation of the product through the reaction of its epoxy groups with the HCl produced in **(a)** (Fig 1).

(a) **(b)**

Figure 1: Scheme of thermal stabilization of PVC films by epoxy groups - **(a)** degradation of film; **(b)** stabilization by epoxidized additive.

Measuring certain parameters, the efficiency of the epoxydation process is industrially monitored, in order to verify if the product meets the specifications of the buyer's market. The analytes water, epoxy and iodine are related with the quantification and consequently to the additive efficiency.

Spectra registered in the near infrared region, ranging from 8500 to 4500 cm^{-1} were used for the construction of multivariate regression models for the above mentioned analytes, with the purpose of minimizing the industrial costs of future analyses.

Partial Least-Squares (PLS) was the chemometric method chosen. The raw data were mean centered and the models were validated by their values of PRESS (Prediction Error Sum of Squares), through cross validation and also using an external data set[1]. The spectra regions used for the calibrations were in the range of 5200-5300 cm^{-1} for water, 4500-5600, 5800-6800 and 7000-7500 cm^{-1} for iodine and 5600-5900, 6900-7000 and 8300-8500 cm^{-1} for epoxy.

The use of PLS for the treatment of this kind of data is highly recommended because, besides being easily applied, it greatly minimizes the time and cost of wet chemistry analyses.

By this methodology, it was possible, through a very simple way, to get regressions with sufficiently low residuals and high coefficient regressions (about 0.98) and to evaluate the spectral regions, which are relevant for each model.

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MICRO-DOMAIN ANALYSIS OF SKIN SAMPLES OF MOOR MUMMIFIED CORPSES BY EVANESCENT WAVE INFRARED SPECTROSCOPY USING SILVER HALIDE FIBRES

P16.13

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Infrared microscopy plays an important role in chemical micro-domain analysis of inhomogeneous materials. IR-microscopes are often equipped with the option of using the attenuated total reflection (ATR) technique. Equipment based on fibre-optics employing bent silver halide fibres of sub-millimeter diameter cross-section is presented which shows promising properties for space resolved measurements with a minimum spot size of 20 x 60 μm^2 tested so far. This system is significantly less complex than a conventional IR-microscope and offers a similar performance at a much lower cost.

The novel accessory yielded a splendid spectral signal-to-noise ratio in particular within the mid-infrared fingerprint region due to optimisation of the throughput by focussing radiation into the fibre and directly coupling it to a liquid nitrogen cooled MCT detector element. It was tested for the analysis of biomedical samples, as the application of infrared spectroscopy in pathology and histochemistry studies has dramatically increased recently. Skin is a rather heterogeneous tissue composed of layers that differ significantly in morphology and composition. As a challenging task, skin specimens and hair samples of ancient corpses preserved by moor or bog conditions were investigated by us. Other interesting samples have previously been characterised, e.g. by Raman spectroscopy (1). The desiccated samples looked leather-like, but were rather brittle, which did not allow the preparation of microtome sections for IR-microscopic studies. Therefore, skin cross sections were analysed using the attenuated total reflection technique with our silver halide fibre loop accessory. Comparable results were obtained with an IR-microscope. In addition, small samples from different locations were analysed by the KBr-pellet technique, embedding the sample in the IR-transparent material. These spectra are comparable to transmission spectra recorded using a diamond anvil micro-cell. Natural dermis samples are mainly composed of collagen, primarily of type I and II. Fibril structure within the mummified samples was still observable by electron-microscopy. Protein and lipid composition was evaluated by comparison with spectra from reference materials.

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P16.14

A RAMAN SPECTROSCOPIC INVESTIGATION OF 5000 YEAR-OLD HUMAN SKELETAL REMAINS

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A Raman spectroscopic study of a red-pigmented human bone (humerus) from a ca. 5000 year old burial site (Jaboticabeira II, close to Laguna, Santa Catarina, south of Brazil) has been undertaken for the first time. This particular bone fragment was found covered with a very thick pigment layer but nearly all bone fragments from this individual were stained. It was not possible to determine the gender from the collected skeletal material but the remains belong to a young adult. Visible (633 nm) and near-infrared (1064 nm) excitation have been used to characterize the pigment and its substrate. The equipment used was a Renishaw Microscope and a Bruker IFS 66 with FRA 106 Raman accessory, respectively.

The red pigment corresponds to hematite (α-Fe_2O_3) [1] which proved to be of a pure form and for which no previous heat treatment processing has been adopted. Apparently its application did not depend on the addition of clays or fine sand as did mediaeval illuminators and artists. The Raman spectra of inner layers in heavily pigmented areas revealed clear evidence of a "limewash" layer which has been applied to the body of the deceased prior to treatment with pigment; this indicates that an ancient technology of lime production from calcite was known to this culture. The clear signs of fires and the natural seashells abundance in the region strongly support this hypothesis, since $CaCO_3$ decomposes into CaO and CO_2 at ca. 800 °C.

Comparisons made with previous Raman studies of bone from ice-mummified biomaterial in a separate excavation [2] indicates that mineralization of the present specimens is well advanced, with evidence of calcium carbonate incorporation into the hydroxyapatite phosphatic matrix.

Concerning the red pigment, a comparison with the practices of North American palaeo-Indian cultures (Seminole Valley, Pecos Culture) [3] at around the same time, reveals the use of the same pigment together in admixture with an unidentified biomaterial, employed for some unspecified purpose but possibly of ritualistic significance.

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QUANTITATIVE INFRARED SPECTROSCOPIC ANALYSIS OF SF_6 DECOMPOSITION PRODUCTS OBTAINED BY ELECTRICAL PARTIAL DISCHARGES AND SPARKS USING PLS-CALIBRATIONS

P16.15

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Infrared spectroscopy is a powerful tool for the analysis of gaseous by-products in sulfur hexafluoride gas resulting from electrical discharges and sparks inside high-voltage equipment. For the production of such samples a custom-made discharge chamber from stainless steel and Teflon was used. The sparks and partial discharges were generated between different point-plane configurations. Various electrode materials used were, e.g., stainless steel, copper, aluminium, silver, tungsten and tungsten/copper alloy. Owing to the different electrical conditions, a wide concentration range of the decomposition products existed. The main-products found were the sulfuroxyfluorides SOF_4, SOF_2 and SO_2F_2. Furthermore, we were able to measure HF following experiments with spark energies in the upper range.

The infrared spectra were recorded using an FTIR-spectrometer equipped with a 10 cm gas cell. Quantification was carried out using partial least-squares with multivariate spectral data from selected intervals. Calibration models were also optimized under the constraint of a minimum number of spectral variables with a view to developing simple infrared photometers based on a restricted number of optical filters or laser wavelengths. Mean squared prediction errors of the different calibration models are reported under the chemometric conditions of using input data from broad spectral intervals or based on a few significant spectral variables. The experimental conditions and practical aspects for reliable quantitative analysis of reactive sulfurfluoride species are discussed.

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P16.16

FIBRE-OPTIC SERS SENSORS

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Surface-enhanced Raman scattering (SERS) has been shown to be a sensitive technique for detecting submonomolecular layers of molecules adsorbed on a great variety of SERS-active surfaces. In combination with optical fibres, SERS can be used for constructing sensitive optical sensors. With such fibre-optic sensors, samples may be analysed remote from the spectrometer, without freely propagating laser light. Furthermore, samples can be exchanged alignment-free and measurements can be taken at difficultly accessible locations.

A fibre-optic SERS sensor can be constructed using the so-called optrode design in which a single fibre or a string of fibres carries both, excitation radiation and Raman-scattered light. Several techniques have been shown to be suitable to modify the fibre tips to become SERS-active and scatter the enhanced signal from adsorbed analytes back into the fibre [1]: slow evaporation of metal island-films, vacuum deposition of metal films over nanoparticles and evaporation of metals on sandblasted or abrasively roughened fibre tips. When coated with the reference chemical thiophenol, all these differently prepared tips have rendered similar SERS enhancements. Therefore, other criteria such as mechanical delicacy, reproducibility or reusability can be considered in choosing the most useful preparation method.

In single-fibre SERS sensors, the SERS signals are superimposed on the Raman scattering from the fibre core. The latter and with it the shot noise of the signal increase with the length of the fibres. Therefore, high signal to noise ratios could so far only be achieved for relatively short fibre sensors or for resonantly scattering samples. Larger enhancements at the fibre tips are required to make longer fibre sensors versatile in chemical analysis. Novel geometrical shapes of the tips are shown here to be a possibility to additionally enhance the SERS signal intensities from such fibre sensors. The tips are polished under inclination angles of 0°, 10°, 20°, 30° and 40° with respect to the fibre cross section and afterwards coated with SERS-active layers. For all above mentioned preparation methods, the SERS signals from the fibre tips increase with the inclination angle. Maximum fibre lengths of up to 1 km are calculated for the detection of thiophenol bands with a signal to noise ratio of 3 at Ag/Al_2O_3 coated fibre tips with 40° inclination. Abrasively roughened fibres with the same inclination of 40° result in somewhat lower SERS intensities, but they offer the advantage of recyclability by dissolving the silver and re-evaporating silver on the fibre tips. Furthermore, a new type of reusable single-fibre SERS sensor is introduced which consists of a conically etched tip coated with silver and shows SERS enhancements exceeding the otherwise prepared tips.

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UTILIZATION OF THE WAVELET REDUCTION FOR INFRARED SPECTRA INTERPRETATION.

P16.17

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Characteristic features of any investigation of industrial infrared spectra in the recognition problem and quantitative relationships are the scarcity of spectral samples and very large its dimensions (several hundred points per spectrum). In accordance with modern notions about the good generalization of mathematical models (based on artificial neural networks too) the ratio of the number of samples in the data set to the number of parameters in the one sample should be kept as large as possible [1]. In these conditions the methods of reduction of data-size for each spectrum are important and frequently inalienable part of construction of satisfactory models. The interesting peculiarity the most of them (especially wavelet transform) is their ability to change correlation between different types of the latent information in the spectrum with truncation. This property can be used to extract particular features from spectra and to improve the quality of the models. In this work we practiced the new approach of utilization of the coefficients of the well-known wavelet transform with the Daubechies basis functions and the Fourier transform for the comparison.

The choice of the modified starches (56 spectra) and the paper coatings (40 samples) was based both on practical importance of these industrial materials and on the importance of their outputs from the mathematical point of view: 9-dimensional output vectors of the starches spectra represented the binary data – 0 and 1; carbonate concentration (L_c) of paper coatings is described by 3 numerical positions – 0, 50 and 100; styrene (L_s) and butadiene (L_b) ones changed in range between 1 and 18. Thus we had the examples for recognition, "intermediate" and quantitative study. The some statistic results are represented in Tables 1 and 2.

Table 1. Satisfactory recognitions for 21 modified starch-samples of the test data set

Complete (528 points)	Fourier (32 points per sample)	Wavelet (26 points per sample)
14 samples (or 67%)	14 samples (or 67%)	2 samples (or 90%)

Table 2. The standard deviation (σ) for the paper coatings test data set (11 samples)

$\sigma(L_s)$	$\sigma(L_b)$	$\sigma(L_c)$	Comments
0.84	0.52	3.34	538 points per spectrum, without reduction, ref. **[2]**
1.72	0.45	1.11	32 points per spectrum, Fourier transform
0.79	0.45	1.63	16 points per spectrum, wavelet transform

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P16.18

BIREFRINGENCE DISPERSION OF POLYMER SOLUTIONS DETERMINED FROM CHANNELED SPECTRA

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Some polymers solved in the thermodynamically "poor" solvents become anisotrope by the supra-molecular order due to the dipolar interactions of their polar side chains [1]. An external electrostatic field increases the solution anisotropy by additional dipolar effects on the polymer side chains.

The system consisting of a such solution layer placed between the crossed polarizers, can modify the spectral composition of the emergent light [2,3]. The channeled spectra obtained with a double beam spectrophotometer [4,5] were used to determine the birefringence dispersion of the polymer anisotrope solutions.

The following relations were obtained to estimate the birefringence Δn and its dispersion $\delta\,(\Delta n)$

$$\Delta n=\frac{1}{2L}\cdot\frac{\nu_{2(k+1)}-\nu_{2k}}{\nu_{2k+1}(\nu_{2(k+1)}+\nu_{2k})-2\cdot\nu_{2(k+1)}\cdot\nu_{2k}} \qquad (1)$$

$$\delta(\Delta n)=\frac{1}{2L}\cdot\frac{2\cdot\nu_{2k+1}-(\nu_{2(k+1)}-\nu_{2k})}{\nu_{2k+1}(\nu_{2(k+1)}+\nu_{2k})-2\cdot\nu_{2(k+1)}\cdot\nu_{2k}}$$

where L is the thickness of the anisotropic layer, ν_{2k}; ν_{2k+1} ; $\nu_{2(k+1)}$ are the wave numbers of the two consecutive channels and of the maximum between them.

The birefringence and its dispersion for poly(phenyl methacrylic) ester of cetyloxybenzoic acid (PPMAECOBA) solved in tetrachloromethane (TCM), was determined from channeled spectra using relations (1). The obtained values do not depend on the molecular weight of the polymer. We have observed the anisotropy of PPMAECOBA only in TCM.

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ABSOLUTE INTENSITIES OF WATER VAPOR LINES IN THE NEAR ULTRAVIOLET AND VISIBLE REGIONS

P16.19

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Although weak in the near ultraviolet and visible regions, the absorption of solar light by water vapor may have, due to the thickness of the atmosphere, significant weight in the earth's radiation balance. In order to improve the knowledge of the water vapor absorption, its spectrum has recently been recorded, from the near ultraviolet to the near infrared, using a high-resolution Fourier transform spectrometer and a long-path White multiple reflection cell [1,2]. With a total absorption path of 602.32 m, the spectral analysis revealed many new lines belonging to the polyads 3ν to 8ν. Most of these lines were successfully assigned [1,2].

Based on these new high-resolution spectra obtained at room temperature, we present, in this work, the absolute intensity of the water vapor lines in the near ultraviolet and the visible regions (26000 – 13000 cm^{-1} spectral range). These intensities were measured using the WSPECTRA program, which fits the observed features with a Voigt profile. With this program, an accuracy of about 1 % on the intensity of a line is generally achieved. Many of the lines measured are, however, very weak and the determination of their parameters is, therefore, subject to larger errors. The line parameters obtained using the above procedure are compared with those collected in the HITRAN database; the extent of disagreement between these two sets of data is analyzed.

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P16.20

NEAR INFRARED SPECTROSCOPY AND MULTIVARIATE REGRESSION TO FOLLOW INDUSTRIAL PROCESS

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A rapid assessment of product quality can often be made using a combination of near infrared spectroscopy (NIR) and multivariate calibration.

The amide **(2)** commercially known as Comperlan KD is a great value in cosmetic industry for its properties as surfactant agents in products which contain this type of compounds in its formulation, such as shampoos, liquid soaps and foams bath. This compound is synthesized from the reaction of amine (diethanolamine) with an ester **(1),** which was originated from the trans esterification of coconut oil according to following scheme.

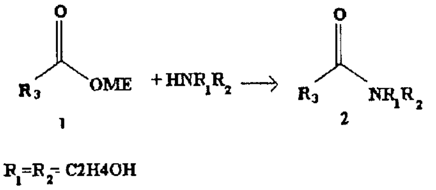

Figure 1- Reaction scheme.

The process is followed by the measured of concentration of free amine to identify the end of process, i.e. the total conversion of ester **(1).**

Through the spectra registered in the near infrared region between 7000 and 4500 cm $^{-1}$ for samples originated from the monitoring of an industrial process, we report the application of the multivariate regression method **PLS** (Partial Least Square) to build the calibration models to quantify the amount of free amine and the yield of amide in the end product.

Different methods to select variables were tested with the aim to find the descriptors which could best predict both analytes. Their performances were assessed using the numerical values of the prediction error sum of squares, PRESS. The regression models were validated by cross validation and external data set.

Near infrared has been proven to be a rapid and accurate technique being an interesting alternative to laborious and time consuming wet chemistry.

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OPTICAL PROPERTIES OF CVD FILMS USED IN MOEMS APLICATIONS

P16.21

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Low-pressure chemical vapour deposition (LPCVD) amorphous silicon oxynitride (a-SiO_xN_y) thin films of various compositions and atmospheric pressure chemical vapour deposition (APCVD) borophosphosilicate glass (BPSG) thin films with different content of phosphorus and bor were investigated. The dependence of the films properties by the deposition temperature and the gas flow ratio was studied by spectroellipsometry (SE) and infrared spectroscopy (IR). The optical properties of these films were pointed out from spectroellipsometric (SE) measurements, by using different theoretical models (as Bruggeman-EMA, Cauchy and Wemple DiDomenico).

The IR spectra shown some molecular vibration frequencies that characterise the film structure. One can be observed a peak with a complex structure, centred on =1000 cm^{-1}, followed by others two at 1400 cm^{-1}, respectively 1600cm^{-1}, assigned with O=N bonds from SiON polymeric chains and the peak from =2335 cm^{-1}- stretching vibration of the Si-H bonds. We have found three peaks assigned to Si-N bonds, Si-O-Si bonds and Si-O bonds from SiO_2. Using Wemple Di Domenico model we have estimate the optical gap for SiO_xN_y film.

We can see that, higher oxygen content in film means a higher optical gap value. This is very important because, in such way, the refractive index and the optical gap values can be controlled during deposition process.

Using Wemple Di Domenico model we found that the optical gap grows with the increasing of boron content in the BPSG films. Via P or B content in the film we can obtain a slow and controlled variation of the refractive index, so we can use these materials for waveguide fabrications.

Using of BPSG as etching mask of silicon offers the advantage of obtaining a silicon surface after etching with lower roughness than in the case of thermal SiO_2 or silicon nitride and oxynitride mask films. The optimal boron content was found to be 9 wt%B.

P16.22

INTERNET ASSISTED EXERCISES IN MOLECULAR SPECTROSCOPY

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The explosive grow of the internet over the past years will not only transform the chemical science but also the chemical education. It is not simply the remote access to certain types of spectrometers, which a typical university can not effort anymore. Remote collaboration clearly extends to mutual exploration of chemical expertise, to scientific data and tools. First lessons learned by sharing instrumentation are about to be extended to expertise and data.

Our work is aimed at the development of multimedia material for Instrumental Analytical Chemistry. The material shall not replace any practical exercise by a virtual laboratory. Instead, it shall enable the student to prepare effectively the real exercises by practising beforehand at virtual instruments and/or by simulating potentially dangerous experiments. Multimedia documents enable the student to progress according to his/her individual needs or abilities, to repeat parts of the material or to include information from other scientific areas. The student will be trained to work interdisciplinary and to combine different techniques, e.g. to apply different spectroscopic techniques in order to solve a given task. The interactive preparatory work at the virtual instrument is shared by the experienced teaching staff. Hazardous situations for people, instrumentation or environment during subsequent labs can largely prevented this way.

Universities from 8 German states together with FIZ CHEMIE BERLIN started a mutual co-operation project, which aims at creating an electronic platform to enable students of different levels, trainees in industry or participants in re-education programmes to access all branches of chemical knowledge in a problem-oriented way. This project is called "Vernetztes Studium – Chemie" (Network for Education - Chemistry). In 1999 it has been approved by the German federal government as one of its priority projects.

Recently we included videoconferencing via internet between our universities. After the Dresden students finished the first part of their task by working out a structural proposal using FTIR, NMR, and mass spectroscopy, they check the validity of their proposed structure by calculating the corresponding spectra via internet using resources at Erlangen. The procedure is directly supervised and commented by staff of both the experimental and the computing labs. The structural formula of each unknown compound suggested by the students is transferred, a 3D structure is generated, and the spectra are calculated using the programme TeleSpec (http://www2.ccc.uni-erlangen.de/research/ir/english/index.html). By comparing the experimental and simulated spectra the students are enabled to judge their results and, if necessary, to revise their proposal.

Last Minute Confirmations...

AUGER-ELECTRON SPECTROSCOPY OF NOBLE GASES UNDER LOW - TEMPERATURE ADSORBTION ON TRANSIENT METALS

P17.1

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One of the effective methods for studing the chemical compounds, gas phase reactions, chemical processes on surface etc. is the Auger-electron spectroscopy [1,2]. Here there are presented the experimental and theoretical Auger-spectra of the noble gases Ar,Xe) obtained under low-temperature adsorbtion on the transient metals (MO, Pd, Ru) surfaces. The experimentally obtained Auger-spectra demonstrate the important role of the outside - atomic relaxation into the energy shift of the lines. In particular, when two holes in the Auger transition appear, the screening processes are determined by the conductivity band electrons for the first adsorbed layer of the noble gas atom, but the relaxation processes for further layers will provided by the polarization of the nearest noble gas atoms.These effects are manifestated more weakly for the Ar atoms in comparison with the Xe atom. This is quantitatively confirmed by the accurate numeral calculations of the Auger-spectra within new consistent approach - the energy approach with the use of the cluster model [2,6]. New Approach is based on combined use of the adiabatic S-matrix Gell-Mann-Low formalism, operator form of the perturbation theory and cluster approach [2,6, 7].

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P17.2

SPECTROSCOPY OF DIATOMIC MOLECULES: ALKALI DIMERS CALCULATIONS. STRONG SPLITING OF FR DIMER 2Π STATE

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Within formally exact perturbation theory with model zeroth density -functional approximation [1], it has been carried out the calculation of the potential curves for the ground and excited states of the diatomic alkali dimers A-B (A,B= Li, Na, K, Cs, Fr). The high-order contributions (due polarization interaction and mutual screening of "above-core" valence quasielectrons) are accounted effectively with the use of a new ab initio functionals. A semiempirical model of the Cohen- Schneider type [5], based on the exactly calculated atomic splittings is given for the treatment of the spin-orbit coupling effects. There have been predicted some unusual especialitites in the spectra of the excited states of the heavy alkali diatomics. The new effect of giant spliting of the Fr dimer 2Π state due to the spin-orbit interaction has been predicted. In table there are presented the calculated values of the spectroscopic constants [T_e –excitation energy (100 cm^{-1}); B_e, ϖ_e- rotation and vibration constants (cm^{-1})] for Rydberg states $n^1\Sigma_g^+$(n=4-6) of Na_2 dimer, calculated by different methods: c - empirical pseudopotential (PP)+core polarization [3]; b – Hartree-Fock ab initio PP + core polarization [4]; d – this work ; a- experiment [2]; We also propose a new fundamental approach to the correct construction of the effective optimal onequasielectron representation for molecules New representation generates the optimal basis for electron structure calculations.

State		$4^1\Sigma_g^+$	$5^1\Sigma_g^1$	$6^1\Sigma_g^+$
T_e	a	283,26	317,72	325,62
	b	285	319	327
	c	286	319	327
	d	285	319	326
B_e	a	0.0899	0,1136	0,1059
	b	0,0838	0,107	0,101
	c	0,088	0,110	0,110
	d	0,090	0,111	0,107
ω_e	a	108,74	109,41	123,67
	b	107	110	119
	c	105	113	123
	d	106	110	120

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LASER-NUCLEAR-MOLECULAR SPECTROSCOPY – NEW TREND IN MOLECULAR SPECTROSCOPY

P17.3

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The following new directions in a laser- nuclear- molecular spectroscopy are considered: the mixed Y-optical quantum transitions; an use of this effect in nuclear – molecular studies with application of lasers; spectroscopy of Y resonances, creation of additional satellites and narrow resonances inside the Doppler contour of Y-line; governing by the intensity of the complicated Y-transitions due to the changing of the molecular excited states population under action of laser radiation [1-2].Under emission or adsorption of the nuclear Y-quantum in molecule there have been taken place a simultaneous changing of the electron, vibration and rotation states. Probability of the molecular vibration or rotation state (in difference from the atomic electron state changing) is not small and must be taken into account even in '0' approximation [1]. Here we present the consistent QED approach to calculation of the electron-nuclear Y transition spectra (set of vibration satellites) of nucleus in the diatomic molecule. The relative intensities of satellites are defined in the relativistic version of the energy approach (S-matrix adiabatic Gell-Mann-Low formalism) [3-5]. QED is needed to describe correctly different channels of the electron-nuclear processes in molecule with explanation of the correctness of transition to non-relativistic limit. For heavy elements systems the fully relativistic approach is of great importance. Within energy approach the decay probability and system excitation probability is connected with imaginary part of the "molecule-field" system. For radiate decays it's manifested as effect of the retarding in interaction and self-action and calculated within QED perturbation theory. When parameter: Z>> 1 (Z~Rm/Mhw, R- the Doppler effect frequency shift, w – vibration frequency, m,M –atomic masses) then insist if the soled lines of the Y-emission or absorption of the nuclei there has been arisen the set of the vibration-nuclear satellites at frequencies E±R (E-nuclear transition energy). They can take all energy from main line. The vibration excitation of molecule with Y-emitted nuclei may compensate the emission (absorption) Y-line shift due to the shaking effect. Some model calculations results are presented [6].

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P17.4

AUGER-ELECTRON SPECTROSCOPY: VALENCE AUGER-SPECTRA AND CHEMICAL BOND, ANALYSIS OF THE ADSORBTION AND GAS PHASE REACTIONS ON SURFACE

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One of the effective methods for study of the chemical bond especialities, the gas phase compositions,gas phase reactions, chemical processes on surface etc. is the Auger-electron spectroscopy [1-3]. In our paper there are presented the experimental and theoretical carbon and nitrogen KVV Auger-spectra obtained under adsorbtion of the CO and NO molecules on the transient metals (MO, Pd, Ru) surfaces [4]. It is experimentally confirmed the general tendency. The nitrogen Auger - spectra of (obtained under low-temperature adsorbtion) are practically fully corresponding to the NO gas phase. However, the oxygen spectra (obtained under heating of the film till 600 K) are similar to the metal oxydes spectra (the dissociative character of the NO low-temperature adsorbtion).

Theoretical calculation of the N (KVV) and O (KVV) spectra are carried out within the non -relativistic version of the energy approach (S-matrix adiabatic formalism Gell-Mann &Low) with the use of the cluster model [4-6]. It is received a good agreement of the experimental and theoretical spectra. It has been proposed the relativistic version for further application to heavy systems. New approach to calculation of Auger-electrons energies adequately accounts the correlation, reativistic and solids effects. In paper there are also examined the possibilities of the chemical analysis with the use of the relations between the core and valence Auger - lines intensities. It's derived a more correct (in comparison with available ones) expressions linking the lines intensities and bond ion character degree (electronegativities) for metal oxydes [7].

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SPECTROSCOPY OF VAN-DER-WAALS MOLECULES: QUASIMOLECULAR TERMS FOR SYSTEMS: "AN INERT GAS ATOM – HALOGEN ATOM", "AN INERT GAS ATOM – RARE EARTH ATOM"

P17.5

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There are presented the results of calculations of the quasimolecular terms (interatomic potentials) for the systems: "an inert gas atom (Ne,Ar,Kr,Xe)- a halogen atom in the ground state (F, Cl, I)" and“ a inert atom (He, Ar)- a rare earth atom (Tm)". The calculations are carried out with use of the effective pseudopotential method (approach similar to the known Baylis method) and the exchange perturbation theory. To take into account the correlation-polarization effects, we propose a new form for polarization pseudopotential. It is obtained on the basis of the effective calculation for the main perturbation theory 'second order'polarization diagrams with the use of the Thomas-Fermi approximation and generalizes the known atomic polarization potential [3]. This DF has not any disadvantages,which are characteristic for the known Dalgarno potential. Some calculated parameters R (interatomic distance: in atomic units) and E (potential well depth: in meV) are presented in table with some experimental data for system: inert gas atom-halogen atom in ground state.

Halohen atom	Parameters	Inert atom Ne	Inert atom Ar	Inert atom Kr	Inert atom Xe
F (X1/2)	E [5]	5,2	12	13	150
	E ths work	6,0	13	16	138
	R [5]	2,8	2,9	3,0	2,3
	R this work	2,9	3,0	3,1	3,2
Cl (X1/2)	E [5]	-	-	-	35
	E ths work	7,2	15	18	32
	R [5]	-	-	-	3,2
	R this work	3,2	3,3	3,4	3,6

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P17.6

MULTI-PHOTON RESONANCES IN MOLECULES, SCATTERING OF LIGHT ON DIATOMIC MOLECULES: QED APPROACH. OPTIMAL ISOTOPE-SELECTIVE VIBRATION LEVELS EXCITATION: THE ISOTOPES SEPARATION

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The consistent unified quantum-electrodynamics (QED) approach has been developed and applied in consideration of the molecular spectroscopy problems. New QED approach is utilized for studing the multiphoton processes in molecules in the laser field.Method bases on a description of molecule in the field by the k-photon absorption lines [1]. The lines are described by their moments of the different orders, which are calculated with the use of the Gell-Mann & Low adiabatic formalism. An imaginary part of the energy shift Im dE(w) determines the transition (decay) probability. It is determined as the central frequency (w) laser pulse function. It has the shape of the resonance corresponding to the (a-p) transition.We calculate for resonance the values:

$$dw(pa|k) = \quad dw \ \mathrm{Im}\ dE(w)(w-w0/k)\ /N ,$$

$$m_n\ (pa|k) = \quad dw \ \mathrm{Im}\ dE(w)(w-w1/k)^n\ /N ,$$

where N is the normalizing multiplier, w0 - the position of the nonshifted line; dw(pa|k)- the line shift under k-photon absorption; w1 =w0 +kdw. The moments m (n=1-3) determine the line center shift, dispersion and asymmetry. QED here used provides the unified correct definition of differne tprocesses channels. Usual nonrelativistic wave functions are used in the concrete estimates. The multiphoton resonances in the SF(6) and CF(3)I molecules are calculated and analysed. It's also proposed new approach to the calculation of the Stark resonances for the molecules,based on the perturbation theory operator method [2]. As example we consider the Stark-resonances for the HCl and CO molecules.

It has been developed the consistent QED theory for the Relay and Raman vibration scattering of the light on the metastable molecular levels. As example the H2, HD, D2 molecules are considered. The polarizability estimates and depolarization degree under Relay and Raman light scattering on the frequencies of neodime and rubidium lasers are presented. The problem of the search for optimal isotope-selective vibration levels excitation scheme (for UF6) is also considered.

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STUDY OF STRUCTURAL PROPERTIES OF CHOLESTERYL ALKANOATES BY FT-IR SPECTROSCOPY

P17.7

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Cholesteryl alkanoates are of considerable importance in biological systems and have been the subject of theoretical and experimental investigations. In this work measured FT-IR spectra of different cholesteryl alkanoates in the solid and liquid state are reported. The behavior of the C=O stretching mode is studied and correlation with the alkyl chain length variations is proposed. The results show a basic disagreement with those using semi-empirical quantum calculation [1] and Raman spectroscopy [2]. To corroborate the present results additional ATR spectra of various cholesteryl alkanoates are measured.

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P17.8

DETERMINATION OF TRIFLUSULFURON METHYL PHOTOPRODUCT BY *LC-MS* AND *NMR* SPECTROSCOPY

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Triflusulfuron methyl (active ingredient of Safari®) is a new selective low use rate sulfonylurea herbicide for the control of many broad-leaved weeds and grasses in sugar beets [1,2]. It has been recently tested successfully in sugar beet in post-emergence control in Morocco.

Trifllusulfuron methyl can undergo either chemical and biological degradation Several reports have indicated that this chemical tend to be persistent in basic soils and could then cause injury to non-target plants [2,3]. Photolysis is considered as only a minor degradation process for this class of herbicides. However, several studies indicate that photodegradation is an alternative pathway to chemical hydrolysis [4].

The photolysis of triflusulfuron methyl (TFSM) was carried out using UV high pressure mercury lamp in aqueous solutions of pH 9 under UV light (λ >290nm) to simulate the sunlight. The reaction followed first-order kinetics. The primary pathway of degradation involves the cleavage of the sulfonylurea bridge. The acidity of the reaction medium increases because of the loss of sulfur dioxide.

Four photoproducts has been detected by HPLC analysis and their molecular weights were determined by LC-MS. The main photoproduct was tentatively identified by LC-MS-MS (APCI) and the structure was confirmed by ^{1}H and ^{13}C NMR.

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