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This conference will cover the following sections:

Section 1: Cryosynthesis, structure and properties of chemical compounds with unusual chemical bonding. Topics: (a) novel cryogenic media clusters and nanostructures; (b) noble gas containing compounds; (b) active intermediate structures, reactivity, and spectroscopy.
Section 2: Novel reaction pathways in cryogenic solids. Topics: (a) reactions in quantum media: liquids, crystals, nanodroplets; (b) cooled biomolecules and cryo-pharmacology; (c) astro- and stratospheric chemistry.
Section 3: Quantum phenomena and reaction dynamics. Topics: (a) coherence and ultrafast dynamics; (b) tunneling and transport processes.

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6-th ICLTC

SIXTH INTERNATIONAL CONFERENCE ON LOW TEMPERATURE CHEMISTRY

ABSTRACTS

As presented by oral and poster contributions,
in Chernogolovka, Russian Federation,
on August 27 – September 1, 2006

SIXTH INTERNATIONAL CONFERENCE ON LOW TEMPERATURE CHEMISTRY
6th ICLTC

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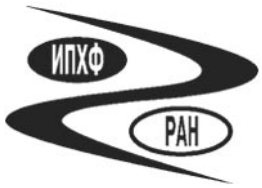

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РОССИЙСКАЯ АКАДЕМИЯ НАУК

ИНСТИТУТ ПРОБЛЕМ ХИМИЧЕСКОЙ ФИЗИКИ
РОССИЙСКОЙ АКАДЕМИИ НАУК

МОСКОВСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ
им. М.В. ЛОМОНОСОВА, ХИМИЧЕСКИЙ ФАКУЛЬТЕТ

ШЕСТАЯ МЕЖДУНАРОДНАЯ КОНФЕРЕНЦИЯ ПО ХИМИИ НИЗКИХ ТЕМПЕРАТУР

ТЕЗИСЫ ДОКЛАДОВ

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Chapter 1

Lectures

Vibrationally Mediated Chemistry in Doped Solid Molecular Hydrogen

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Matrix isolation spectroscopy is a proven method used to study reactive species [1, 2]. The desirable characteristics of a matrix host being inertness and optical transparency lead most naturally to the use of rare gas atoms as matrix hosts. Although the chemical inertness of rare gas matrices is unrivalled, isolation of reactive species in cryogenic solid parahydrogen (pH_2) offers several advantages and new possibilities [3, 4]. While the "cage effect" is a central concept in photochemical studies of molecules embedded in rare gas crystalline solids,[2–5] the cage effect is negligible in solid pH_2 due to the light mass of H_2 and large amplitude translational zero-point motion of the pH_2 matrix [4]. The minimal cage effect allows *in situ* photodissociation of molecular precursors to be used as an effective means to generate reactive species trapped in solid pH_2. This paper will utilize the 355 nm photodissociation of Cl_2 trapped in solid pH_2 at 2 K to form isolated Cl photofragments. At these low temperatures ($kT \approx 1.4$ cm^{-1}) the Cl atoms can not react with the pH_2 host since the reaction Cl + H_2(v=0, j=0) → HCl(v=0, j=0) + H is endothermic by +360 cm^{-1}. Irradiation of the Cl atom doped pH_2 solid with broadband infrared (IR) radiation from 4000 to 5000 cm^{-1} induces reaction of atomic Cl with the pH_2 matrix to form HCl. The infrared induced chemistry is attributed to near-IR absorptions of solid pH_2 that lead to the creation of H_2(v=1) vibrons which supply the energy necessary to induce reaction. The kinetics of this low temperature IR induced reaction is investigated using Fourier transform infrared spectroscopy of the HCl reaction product and the $^2P_{1/2} \leftarrow {}^2P_{3/2}$ transition of the Cl reagent. Experimental results for photochemical studies conducted in solid *para*H_2, *ortho*D_2, and HD will be presented and discussed.

The UV laser system used in this work was purchased with funds from the United States Air Force Office of Scientific Research (F49620-2-1-0204). This research was sponsored by the Chemistry Division of the National Science Foundation (CHE 03-16268).

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The making of Schrodinger's cats and their observation in phase space

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Understanding the extent of quantum coherence in condensed media is of both fundamental and applied interest: The process of decoherence – the collapse of the quantum and emergence of the classical – is not trivial to describe, especially in strongly coupled systems. Yet Q-coherence is key to control, which is already in practice. I will describe time-frequency-resolved, multi-color, four-wave mixing measurements designed to prepare and interrogate coherences in the most direct way: a direct imaging of off diagonal densities ρ_{12}. While such measurements are most conveniently carried out in energy representation, the preferred basis is trickier to define, or extract. I will present the methods for preparation and interrogation of coherences, and will give examples of long lived coherences that involve a significant number of independent degrees of freedom, which fit the description of Schrodinger's kittens, if not "cats". Implementations in a variety of systems will be highlighted, the most instructive of which remain studies in rare gas solids.

Spectrally- and Time-Resolved Sum Frequency Generation (STiR-SFG): a new tool for ultrafast dynamics at interfaces

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This talk will review the new femtosecond spectroscopic techniques developed in our group for studies of ultrafast dynamics at surfaces and interfaces. The recently developed spectrally- and time-resolved Sum Frequency Generation (STiR-SFG) is a surface-selective 3-wave mixing (IR+visible) capable of measuring spectral evolution of vibrational coherences on sub-100 fs time scale. A detailed description of this technique will be presented, and a noniterative method for deconvolution of the laser pulses will be introduced to obtain the molecular response function. The approach is also generalized to XFROG (cross-correlation Frequency Resolved Optical Gating) deconvolution, a common problem in ultrafast pulse characterization. Application of STiR-SFG to hydrogen bonding dynamics at aqueous interfaces will be discussed. Spectral dynamics of the OH (OD) stretch vibration on the 50-150 fs time scale provides real-time observation of ultrafast H-bond rearrangement. Tuning the IR pulse wavelength to the blue or red side of the OD-stretch transition, we selectively monitor the dynamics of different sub-ensembles in the distribution of the H-bond structures. The blue-side excitation (weaker H-bonding) shows monotonic red-shift of ν(OD) frequency. In contrast, the red-side excitation (stronger H-bonding structures) produces a blue-shift and a recursion, which may indicate the presence of an underdamped intermolecular mode of interfacial water.

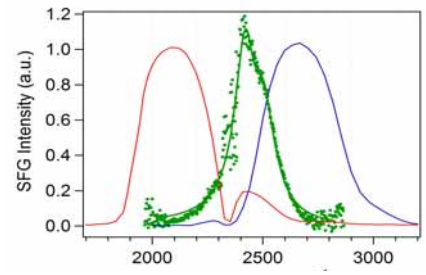

Fig. 1. Frequency-domain SFG spectrum of the ν(OD) transition of D_2O at CaF_2 interface (green dots – experimental data, green line- fit). IR pulse spectra used for the Spectrally- and Time-Resolved SFG measurements (STiR-SFG) are shown in thin blue and red lines.

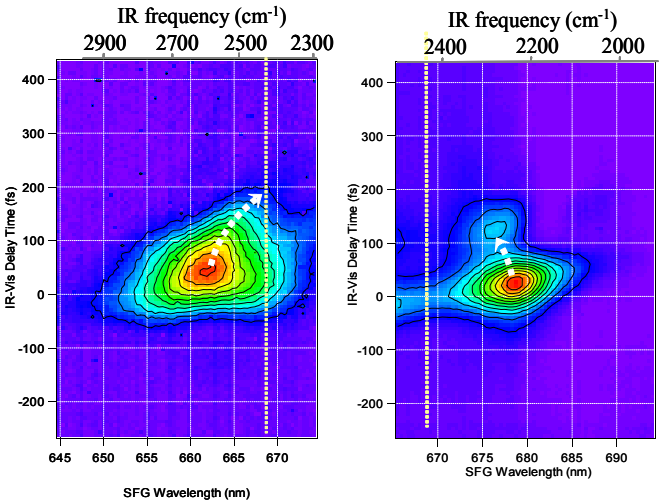

Fig. 2. Spectrally- and Time-Resolved SFG of D_2O at CaF_2 interface. Left: IR excitation 2650 cm^{-1} (blue side). Right: IR excitation 2200 cm^{-1} (red side). Vertical axis: IR-visible delay time (fs), horizontal axis: SFG wavelength.

Coherent-incoherent transitions in low-temperature chemical dynamics

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The rate constant can be introduced only if coherent transitions in the chosen pair of initial and final states is replaced by the exponential decay of the initial state population when transitions from the system to the sufficiently wide manifold of final states (reservoir) suppress recurrences. The irreversibility criterion states that this decay occurs if the level spacing in the reservoir spectrum Ω becomes smaller than the mean transition matrix element $C = \langle C_{if} \rangle$. The Heisenberg equations of coupled motion of the system and reservoir are shown to reduce to the integral Langevin-type equation for the system evolution. This equation demonstrates that the wide intermediate region with more complicated dynamics exists between the coherent oscillation and exponential decay regimes. The following representative examples have been studied.

1. Vibrational relaxation and recovery in the one-level system.

In the weak coupling limit ($C << \Omega$) transitions between the system level and reservoir resonant level are coherent, and the amplitude of the system state is $a(t) \approx \cos(Ct)$. In the strong coupling limit, $a(t)$ has the form of soliton-like pulses with periodicity $2\pi/\Omega$ and characteristic time, defined by the Fermi Golden Rule for the transition probability: $a(t) \approx \exp\left(-\pi C^2 \Omega^{-1} \left| t - 2\pi n \Omega^{-1} \right| \right)$, $n = 0,1,\ldots$. The recurrence period (identified as Poincare cycle period due to quantum-classical correspondence), determining the system-reservoir energy exchange, increases with increasing density of the reservoir states.

2. Vibrational relaxation and phonon echo.

If the decay rate for the quasi-stationary state of a system (decay is induced by an external mechanism) is smaller than Ω but exceeds the system-reservoir transition probability, damped oscillations proceed between resonant states. If $\pi C^2 / \Omega > \Omega > \Gamma$, the recovery of the initial state leads to the phonon echo in each Poincare cycle with the periodicity $2\pi/\Omega$. System-reservoir exchange suppresses the intrinsic decay in the system.

3. Dissipative tunneling in two-level system (TLS).

If TLS splitting is smaller than TLS-reservoir transition probability $\pi C^2 \Omega^{-1} > \Delta, \Omega$, coherent tunneling is replaced by dissipative one. If $\Delta > \Omega$, $a(t)$ decreases in the successive Poincare cycles.

4. Strongly asymmetric double-well potential.

Ttunneling transitions takes place from one initial state of a shallow well to the set of the final states of the deep well with sufficiently dense spectrum. The coherence destroy results from the interference between final states which suppresses the inverse transitions and is accompanied by the tunneling-induced relaxation in the deep well. Poincare cycle periodicity is defined by the level spacing.

5. Nonadiabatic transitions.

Several coherent-incoherent transitions are characteristic for transitions between crossing diabatic potentials. This behavior arises due to oscillating behavior of the Landau-Zener transition probability as function of the adiabatic coupling strength.

The applications of the above models to the vibration –tunneling spectra and low-temperature relaxation of non-rigid molecules are discussed.

Since the parameters of both system and reservoir states depend on reduced masses, the mode specific behavior and anomalous isotope effects are predicted.

Gas Phase Reaction Kinetics at very low Temperatures: Recent advances on the carbon chemistry using the CRESU technique

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Understanding the different processes that are involved in the formation and destruction of molecules in planetary atmospheres and interstellar clouds is still a great challenge for astrochemists. Modelling the chemistry of these very cold environments (75 K for the atmosphere of Titan [1], 40 K for Pluto and ~10 K for dense interstellar clouds [2]) requires the knowledge of a great number of physical and chemical data such as the UV radiation field, the cosmic ray flux, inelastic collision and chemical rate coefficients as well as branching ratios of these processes. Of particular interest is the understanding of how complex molecules such as $HC_{11}N$ or unstable hydrocarbons can survive in such extreme environments.

Recently, we have used the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in a Uniform Supersonic Flow) technique to study the reactivity of carbon-based molecules such as CH, C_2, C_4H, anthracene $C_{14}H_{10}$ and several saturated and unsaturated hydrocarbons. We have demonstrated that the reactivity of $C_{14}H_{10}$ with OH [3] and CH [4] is very efficient in the temperature range 58 – 470 K. This is also the case for the reactivity of $C_2(^1\Sigma_g^+)$ [5], $C_2(a^3\Pi_u)$ and C_4H with several small hydrocarbons in the temperature range 24–300 K. These processes can contribute to the increase of complexity by carbon insertion for example in the studied hydrocarbons. The temperature dependence of these reactions will be presented at the conference.

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Spectroscopy and Dynamics in Solid Parahydrogen

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Reports from several groups describing the rovibrational spectroscopy of small molecules isolated in solid parahydrogen (pH_2) have begun to illuminate the unique rotational dynamics obtained in quantum solids, e.g.: the first observation of nearly free rotation in a solid by non-hydride dopant species. Moreover, detailed analysis of spectra of six CO isotopomers in pH_2 reveals clear trends that cannot be explained by existing models developed to describe molecular rotations in classical solids. Instead, the rotational dynamics appears more closely related to that for small molecules in quantum liquids.

Hydrogen Atoms in Solid Xenon: From Simple Dynamics to Novel Chemistry

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Trapping of hydrogen atoms in a solid xenon matrix was first documented more than forty years ago [1]. Nevertheless, after numerous studies, the nature of traps and the fate of hydrogen atoms upon annealing are still under discussion. According to the EPR data, hydrogen atoms in xenon become mobile at around 40 K, that is, well below matrix softening temperature. This feature makes it possible to use xenon matrix for model studies of diffusion and chemical reactions of H atoms in low-temperature solids. In the paste decade, physical and chemical dynamics of hydrogen atoms in xenon has attracted considerable interest due to discovery of novel unusual species – xenon hydrides [2] and demonstration of the role of hydrogen atoms in their formation [3].

This talk will present an overview of recent studies of trapping and reactions of hydrogen atoms produced by fast electron irradiation of guest molecules in solid xenon, which were carried out in our laboratory using a combination of EPR and IR absorption spectroscopy. It will be focused mainly on two aspects. The first one is concerned with trap structure and evolution of local environment of H atoms in xenon, which will be analyzed in detail on the basis of EPR experiments in matrices of different isotopic composition. In particular, using a unique diamagnetic ^{136}Xe matrix provides superior resolution and sensitivity (like in argon) due to absence of magnetic matrix line broadening. Doping of this matrix with small amounts of a magnetic ^{129}Xe isotope makes it possible to probe the local environment of trapped H atoms and its changing upon annealing. Second aspect deals with the chemistry of H atoms in solid xenon. The combined spectroscopic approach (EPR + FTIR spectroscopy) allowed us to determine quantitative contributions of different reaction channels, including hydrogen abstraction, addition to double bonds and formation of xenon hydrides (HXeH and HXeY). In most cases, it was possible to monitor the formation of all the reaction products directly. It was found that the reactions under consideration were controlled by hydrogen atom diffusion in solid xenon, so the product distribution was determined by relative concentration of various reactive species in matrix. Finally, the prospects of controlled synthesis of novel species using reactions of mobile hydrogen atoms in xenon will be outlined.

This work was supported by the Russian Academy of Sciences (programme no.1 of the Branch of Chemistry and Material Sciences).

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Ultrafast Dynamics of Electronic State Populations in Matrix Photochemistry

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The photochemical dynamics of the molecules FCl and F_2 embedded in clusters and in solid argon is explored by semiclassical simulation methods. The focus is on the role of each of the multiple electronic states that participate in the process, on the transitions between these states and on the consequences of the transitions for the dynamics of the atoms on the femtosecond timescale. The results show that the dynamics of electronic transitions plays a key role in the mechanisms of photodissociation, recombination, and molecule-to-matrix energy transfer. A result of major interest is the occurrence of ultrafast spin-flip processes in these systems, that lead to population of Π triplet states within less than 50 femtoseconds. This raises interesting possibilities of control of ultrafast spin-flip processes.

Another interesting finding is that there are very different propensities for states of different angular momentum quantum numbers Λ and Ω. The simulations suggest physical insights for these properties.

The results provide new understanding for the role of electronic states in condensed-phase photochemistry. The research is done in cooperation with the groups of Professor J. Manz and Professor N. Schwentner of FU Berlin.

Spectrally resolved transient grating studies of gas hydrates

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Vibronic dynamics of molecules isolated in the model solids of rare gas matrices has been investigated at some depth. The extension of the science learned there, to molecular solids, is of great interest. Gas hydrates provide an opportunity for systematic investigations of molecules trapped in a lattice of water molecules, from the ordered crystalline structures of the clathrates to disordered ice. To interrogate energetics and vibronic dynamics in this important class of solids, in which electronic quenching precludes the possibility of fluorescence based spectroscopic interrogation, we rely on spectrally resolved transient grating measurements. I will highlight the information content in this incisive tool, using bromine hydrates as example.

All resonant, spectrally-resolved, transient grating measurements of Br_2 hydrates allow the preparation of vibrational packets in the $B(^3\Pi_{0u})$ state, and the direct imaging of the packet in a time vs. frequency dimensions. The images can be inverted to coordinate-time domain, from which detailed information about dissipation, cage relaxation, and solvation energetics of electronic states is obtained. Independent of initial excitation energy, for a range of excitation energies in excess of the binding of $Br_2(B)$, the packet is always formed near the bottom of the potential and undergoes coherent oscillations for many periods. This can be understood along with the strongly perturbed absorption spectra of hydrated Br_2 in terms of coupled guest-host excitation, and strong electronic pre-dissociation. The contrast with rare gas matrices is dramatic, and will be highlighted. On longer time scales, thermalization and acoustic scattering of the solids is extracted from the same measurements, data that is important in understanding thermal conductivity and stability of clathrates.

Electronic excitation of matrix and impurity states under excess electron drift through solid xenon

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The reduced mobility of excess electron in solid xenon is more than 10^3 times higher (it becomes more than in metallic silver) and the elastic losses are as much lower than those in Xe gas. Together with penetrability of solid xenon for the electric field that makes it possible to accelerate the excess electrons there up to the energies sufficient for molecular-like Xe_2 exciton formation. However the electron energy expenses for the generation of excitons, which quickly decayed by VUV photon emission, impede the further electron overheating up to the matrix ionization threshold thus preventing bulky electrical discharge rise. It is very important for practice that the electrical discharge supplied the cheap free electrons may be anyway organized in solid Xe by using three-electrode cell with photocathode sensitive to exciton luminescence at 172 *nm* and cathode-grid gap filled by few mbar of Ar (Xe crystal is grown at the bottom in grid-anode gap). The discharge occurred for the account of the positive feedback *via* photoelectron emission and electron avalanche in cathode-grid space appeared at voltage of several hundred *V* per *mm*. It is accompanied by intensive emission both in VUV and in visible, last because of trace impurities with concentration about 1 *ppb*.

The efficiency of the electrostatic energy conversion directly into VUV light is as high as 20% in our experiments. Provided the very small amounts of impurities were solute in Xe their plasmochemical reactions initiated by free electrons with energy up to 8 *eV* can be observed, both reagents and products are matrix isolated in solid Xe at low temperature. Such kind of initiation is much more promising than photochemical excitation. First it is not necessary to use only the chemicals possessed intensive absorption in optical range, and second, the probability of drifting electron interaction with the reagent is three order of magnitude more than that of photon because the electron path in the sample is 10^3 times more than its thickness.

The high outer pressure effects will be discussed as well. The first is the transition from two-center exciton Xe^*_2 to spherically symmetric Xe^*_{13} at pressure when interatomic distance in a solid becomes equal to that in Xe^*_2. Besides since the energy required for free electron formation decreases while the exciton energy contrary increases with outer pressure growth the correspondent curves should cross at some pressure leading to the critical phenomenon tractable as the “insulator – semiconductor” phase transition.

The similar behavior should be characteristic as well for Kr and Ar matrices.

This study has been supported in part by Russian Foundation for Basic Researches, Grant # 04-03-32684.

Matrix isolation and computational study of the photochemistry of polysulfur-nitrogen heterocycles

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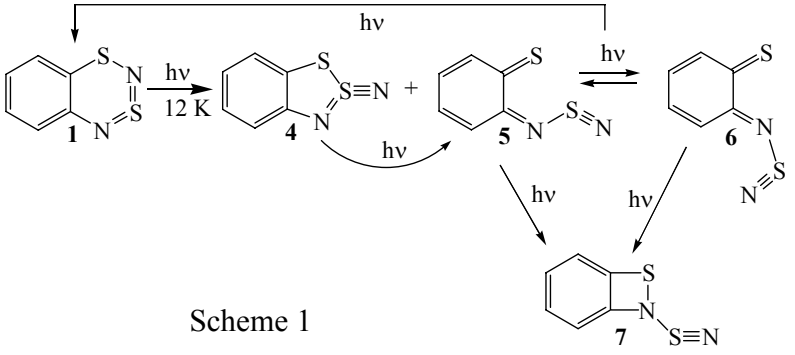
An extensive family of polysulfur-nitrogen heterocycles including both closed- and open-shell structures has recently been discovered [1–4]. In particular, the open-shell structures, especially stable heterocyclic π-radicals, have emerged as attractive building blocks for molecular magnets and / or molecular conductors.[2]

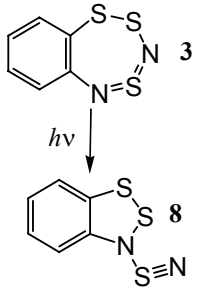
Recently [3–4], we have discovered that thermolysis and photolysis of heterocycles **1** and **2** afford *stable* 1,2,3-benzodithiazolyl radicals (**2),** identified by ESR spectroscopy. These processes can be considered as particular cases of previously unmentioned trend of polysulfur-nitrogen heterocycles to form *stable* thiazyl π-radicals.

To reveal the mechanisms of these unique photoreactions, the photochemistry of 1,3,2,4-benzodithiadiazine (**1a**) and 1,2,4,3,5-benzotrithiadiazepine (**3**) was studied in Ar matrices at 12 K using IR and UV-spectroscopy as well as computational methods (DFT and CASSCF/CASPT2).

In both cases, the primary processes were found to be the dissociation of a weak SN bond followed by the formation of a series of products in the case of **1** (Scheme 1) and the only product with a five-membered heterocyclic structure (**8**) in the case of **3** (Scheme 2). In the former case the intermediates can be mutually interconverted as well as converted into the starting compound **1** with a selective irradiation.



Scheme 1



Scheme 2

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Tunneling Exchange Chemical Reactions of Matrix Isolated Hydrogen and Deuterium Atoms

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The exchange tunneling reactions in which deuterium atoms replace the hydrogen atoms in H_2 or HD molecules in impurity-helium solids were first discovered in Chernogolovka by Gordon *et al.* [1]. Comprehensive studies of kinetics of these reactions were performed by Ivliev *et al*. [2] and Tsuruta *et al*. [3] in solid molecular matrices and later by Kiselev *et al.* [4] in impurity-helium solids.

We present results of continuous wave and pulse electron spin resonance (ESR) studies of the kinetics of tunneling exchange chemical reactions of hydrogen isotopes in impurity-helium solids. Our two pulse electron spin echo envelope modulation (ESEEM) measurements show that 50-60% of stabilized atoms reside on the surfaces of molecular nanoclusters which form impurity-helium solids. We studied the changes in the immediate molecular environment of the H and D atoms during the course of tunneling reactions [5].

We also present studies of the kinetics of H atom recombination in thin solid H_2 films at temperatures less than 1 K [6]. It was found that at temperatures $0.3<T<0.9$ K the recombination rate constant is far smaller than predicted theoretically[7] and verified in experiment for higher temperatures [8]. For temperatures $T<0.15$ K concentrations of H atoms of order 10^{18} cm^{-3} were very stable during two weeks of observation. This leads to a vanishingly small heat release, which makes it possible to achieve extremely low temperatures for this metastable system, enabling studies of possible Bose-Einstein condensation of H atoms in solid H_2.

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Light-induced rotational isomerization of small molecules in noble-gas matrices

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The rotational isomerization (rotamerization) of matrix-isolated molecules can be efficiently produced by their vibrational excitation. The matrix-site selectivity of the light-induced rotamerization process was first demonstrated for HONO and $(FCO)_2$ [1,2]. This observation shows that the rotamerization process is promoted by the direct vibrational excitation of the molecule, and non-resonant energy flow in the matrix is of minor importance. It follows that the rotamerization upon narrow-band tunable excitation can be a tool of reactive vibrational excitation spectroscopy [3–5].

The experiments with selective vibrational excitation provide data aiding the identification of various molecular conformers as it was demonstrated for oxalic (HOOCCOOH), malonic ($HOOCCH_2COOH$), and maleic (HOOCCH=CHCOOH) acids [3,4,6]. By optical pumping of the ground-state *trans* conformers, the higher-energy *cis* forms of formic (HCOOH), acetic (CH_3COOH), and propionic (CH_3CH_2COOH) acids were prepared [7–9]. The *trans* to *cis* conversion can be achieved even if the pumping energy is somewhat below the predicted reaction barrier, and a tunneling mechanism was suggested for this effect [10].

For formic, acetic, and propionic acids, the higher energy *cis* conformer decays back to the ground state *trans* conformer via a tunneling mechanism, and the *cis* to *trans* tunneling rates of these species show remarkable host and temperature dependencies [11–13]. The quantum yields of IR-induced rotational isomerization were measured for these species in various noble-gas matrixes [5,12,13]. The comparison of the results obtained for these three acids and recently for propiolic acid (HCCCOOH) [14] develops the understanding of mechanisms involved in intramolecular vibrational energy redistribution in the solid phase, however, a number of observations have no interpretation yet. As the most recent result, we discuss rotamerization in formic acid dimers [15].

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Regularities of electron transfer reactions in proteins at low temperatures

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The electron transfer (ET) reactions between donor and acceptor centers in proteins are very suitable for investigation of the role played by the structure and dynamics of the intervenient medium in ET processes. In the case of proteins with known structures, one could investigate the ET kinetics between donor and acceptor centers fixed in the protein structure at a given distance with known separating and surrounding atomic groups. This gives a possibility for application of published theoretical models and for development of new approaches [1-4] to determine quantum and dynamical peculiarities of the protein matrix as a highly organized macromolecular system.

Here, the electron transfer in the reaction center from *Rps. viridis* has been investigated experimentally in the range of temperatures from 153 to 295 K. The kinetics of the ET reaction from the proximal heme of cytochrome to the special pair has been found to be non-exponential. The degree of non-exponentiality strongly depends on temperature, with increasing non-exponentiality at lower temperatures. The experimental kinetic data are analyzed in frames of a new theoretical model, based on Ovchinnikova-Helman-Sumi-Marcus approximations, which allows establishing a connection between the observed kinetic curves and structural dynamics of the protein. The phenomenological model subdivides the multi-time-scale dynamics of the protein into two groups: fast and slow. The division is determined by the rate of electron transfer, which is dynamically controlled by the slow modes of the protein medium. The slow modes are described by a generalized collective coordinate X , for which a diffusion type of dynamics is assumed. The analysis of the temperature dependence of the kinetic curves allows a complete characterization of the slow time-scale protein dynamics: we find the corresponding activation barrier for the dynamics of X to be around 0.5 eV. We discuss the nature of the collective modes X and the nature of its activation barrier (breaking of hydrogen bonds). The main conclusion is that the ET kinetics at low temperatures can be used as a probe of protein structural dynamics on the microsecond time scale.

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Formation of H_6^+ ion and its isotope substitution processes in irradiated solid parahydrogen

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Ten years ago, we found quartet ESR lines with hyperfine coupling constant A = 20.44 mT and g = 2.0021 in γ-ray irradiated solid para-H_2. We previously assigned them to H_2^- but theoretical calculations have supported neither its stability nor ESR parameters observed. We recently proposed the quartet lines should be reassigned to H_6^+.

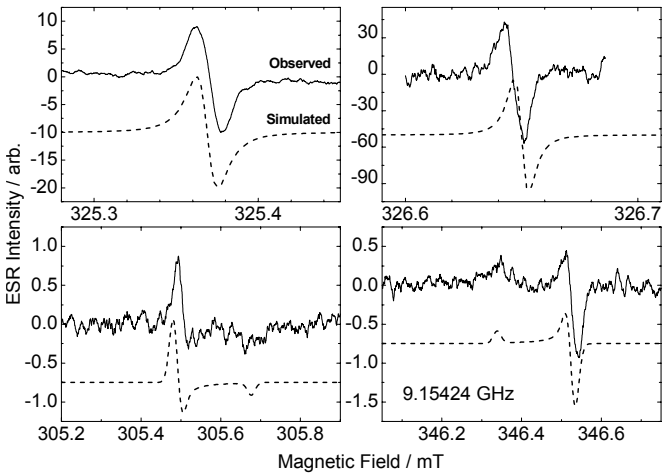

Fig. 1 The quartet ESR lines.

We carried out ab initio molecular orbital calculations for H_6^+. The H_6^+ ion composed of H_2^+ core sandwiched between two side-on H_2 to form $H_2(H_2^+)H_2$, being lower in energy than H--H_3^+--H_2 van der Waals complex by 0.16 eV. We also found that six is the magic number. Since additional H_2 molecules only physically bound to H_6^+ to form H_6^+-$(H_2)_n$ complex, positive charge of H_6^+ does not delocalize in solid hydrogen. ESR g-value, and hyperfine coupling constant of core H_2^+ and H_2 ligands of H_6^+ were calculated to be g = 2.0022, A_{H2+} = 20.08 mT, and A_{sid} = 10.26 mT. The quartet ESR lines observed should be H_6^+ composed of H_2^+ and two side-on para-H_2 ligands rotating almost freely around the main axis. We very recently found ESR signals of its isotope substituent, $H_2(H_2^+)D_2$, $D_2(H_2^+)D_2$, $H_2(H_2^+)HD$, and $H_2(HD^+)H_2$ in irradiated solid para-H_2-D_2 and para-H_2-HD mixtures. They confirm the new assignment to H_6^+.

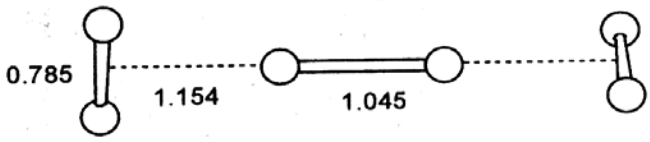

Fig. 2 Optimized geometry of H_6^+

The H_6^+ ions are probably produced by

$$H_2^+ + 2H_2 + M \rightarrow H_6^+ + M \quad \text{or} \quad H_3^+ + H + H_2 + M \rightarrow H_6^+ + M$$

reactions which are difficult to take place in gas phase because of four body reactions. On the other hand, these reactions proceed much more effectively in solid H_2 because of abundant H_2 (and M) nearby H_2^+ and H_3^+.

Charged Particles in Liquid and Solid Hydrogen

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The review report is devoted to the results of our studies of diffusion of positively or negatively charged nanoparticles (charges) created under β-irradiation in condensed H_2 and D_2 at low temperatures and pressures P≤ 100 atm. It includes also the results of our recent experimental and theoretical studies of the nonlinear waves and capillary turbulence at the positively charged surface of liquid hydrogen. Charged particles were created in a thin layer of condensed hydrogen (about 10 μm) near the surface of radioactive target – molybdenum disc covered with a tritium-titanium film. The mean energy of β-particles was ~5 keV. The sign of the charges moving through the sample of liquid or solid hydrogen was determined by the sign of the applied external electric field. From measurements of the mobility of charges in liquid hydrogen and observations of the charge penetration through the liquid-gas interface it was established that 3 types of charged particles can be created in liquid hydrogen: positively charged snow balls, consisted of the molecular ion surrounded by a layer of solidified hydrogen, and negatively charged particles - electron bubbles and negatively charged hydrogen snow balls. In solid hydrogen we could distinguish only 2 types of charged particles - positively charged snow balls and of the negatively charged electron bubbles.

The experiments in solid hydrogen had shown that in solid samples grown from the *normal hydrogen* mobility of positive and negative charges depended strongly on the ortho-para content of the sample. More over the time dependence of mobility of the both charges had reproduced the known from literature curve of ortho-para conversion in condensed hydrogen. The reasons for these changes in charge mobility are under discussion till now. From comparison of the value and the temperature dependences of diffusion coefficients of different point defects in samples, grown at small pressures from pure para-hydrogen –the ortho-molecules (self diffusion) and the electron bubbles, one can conclude that diffusion of the both the defects is controlled by their interaction with thermal vacancies (vacancy-assisted motion). At temperatures above 10 K the effective energy of activation of diffusion of both the defects is close to the sum of the energy of creation the vacancies and the height of the potential barrier for their thermally activated jumps from site to site. Below 10 K the effective activation energy of the defects lowers near twice. It indicates to significant changes in the mechanism of motion of the thermal vacancies - from thermally activated diffusion above 10 K to quantum tunneling at low temperatures.

The possibility to create the two dimensional layer of positive charges below the surface of liquid hydrogen had allowed us to use the new method of generation of capillary waves at the surface of liquid and to investigate widely a number of very interesting phenomena (like the reconstruction of the charged surface in strong electric fields, the capillary turbulence formation and decay, etc.) at the surface of liquid hydrogen.

Matrix stabilization of active intermediates. Classic and new way on study of reaction mechanisms and dynamics

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The absence of translational mobility of radicals is one of the main and obvious advantages of the matrix isolation technique. This is, however, a serious drawback at the same time for it restricts applicability of this technique for studying bimolecular reactions, dissociation reactions, etc. Another source of restriction is the high values of activation energy for monomolecular reactions, which for many types of radicals are 60-100 kJ/mol. Therefore, such radicals although being potentially active in the reactions of recombination, abstraction or substitution, may still remain inert in absence of reactive surroundings at room (or higher) temperature. Meanwhile the surface of a mineral carrier provided an opportunity to create defects of various natures, i.e., paramagnetic. Indeed, the presence of these defects has led to the generation on the surface of structurally different grafted radicals in the reactions of addition and other processes. Silica surface meets the main requirements for these types of surfaces, such as high bond energy of the carrier to provide its chemical innocence, and relative isolation of the defects produced to exclude inter-defect interaction.

Our investigation demonstrated plausibility of this approach in generation of various types of grafted radicals in the course of mechanism investigation of both thermal radical reactions (C-centered radicals and SO_2) and photochemical reactions (of allyl, nitroxyl and peroxy radicals). We will discuss the results of the investigations into photochemical transformation of grafted peroxy ($\equiv SiOCH_2OO^{\bullet}$, $\equiv SiOCH_2CH_2OO^{\bullet}$, $\equiv SiCH_2CH_2OO^{\bullet}$ and $\equiv SiOCH_2CH_2OCH_2OO^{\bullet}$) and nitroxyl ($\equiv SiON(O^{\bullet})CH_3$, $\equiv SiO(CH_2)_nCH_2ON(O^{\bullet})CH_3$, $\equiv SiO(CH_2)_nCH_2N(O^{\bullet})CH_3$, where n = 0,1, and $=Si(OH)OCH_2N(O^{\bullet})OCH_3$) radicals. In the latter case, molecular dynamics has been studied both in presence and in absence of the adsorbate (CO_2) on the surface. It has been shown that the photochemical dissociation of alkylperoxy radicals takes place via two channels: via O-O vs. C-O dissociation. It has been established, that the direction of the transformation depends on the state of the activated aerosil, which in its turn depends on the way of preparation of the radical. For example, for the $\equiv SiOCH_2CH_2OO^{\bullet}$ radicals it is possible to change the ration between the channels by 30-40 times. Established, that crafted radicals of nitroxyl type upon excitation into $n\rightarrow\pi^*$ transition (436 nm, 77K) dissociate along O-N or C-N bonds with the quantum yields ≈0.6 (O-N in $\equiv SiON(O^{\bullet})CH_3$), ≈0.02 (O-N in $=Si(OH)OCH_2N(O^{\bullet})OCH_3$) and ≈0.002 (C-N in $\equiv SiOCH_2CH_2N(O^{\bullet})CH_3$).

Analysis of molecular dynamics of various “spacer-free” radicals grafted on silica surface allowed to obtain characteristic values of rotational correlation and to elucidate the influence of the absorption layers on the dynamics of their transformations. It has been shown that the nature of the rotational mobility of ≡SiOC$^{\bullet}$O radicals change from anisotropic one to the Brownian one in the absence of the adsorbate to Brownian within the potential range ≈1.7÷1.9 kcal/mol upon formation of the adsorption layer on the surface of the aerosil. The variations in the line broadness of the hyperfine splitting in multiproton radical ≡SiOC$^{\bullet}$$(CH_3)_2$ has been experimentally registered for the first time; the activation energy of the rotation of methyl group (1.1 kcal/mol) and pre-exponential factor for this type of movement (2×10^{11} s^{-1}) have been determined.

This work was financially supported by Russian Foundation for Basic Research.

Chemical Reactions in quantum matrices. What can we learn?

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Solid parahydrogen is an excellent matrix not only for high-resolution infrared spectroscopy, but also for the study of chemical reactions at low temperatures [1,2]. Weak interaction in solid parahydrogen makes rotational motion of dopant molecules well quantized as in the gas phase. In addition, due to the softness of the quantum crystal, a variety of chemical reactions at very low temperature can be studies in solid hydrogen. Quantitative information on chemical reactions of nearly free molecules at liquid He temperatures such as tunneling chemical reactions can be obtained directly from the spectroscopy of molecules in solid parahydrogen.

In the present work, we focus on chemical reactions that take place in solid hydrogen. Matrix isolation spectroscopy in solid parahydrogen has many advantages over other techniques in studying chemical reaction dynamics at low temperatures. Molecules in solid parahydrogen at liquid He temperatures occupy only a limited number of its rotational levels, mostly the J=0 ground rotational level only. Therefore, reactions in solid parahydrogen themselves can be considered as state selective reactions, which give us quantitative information on the state dependent phenomena for a variety of reactions. As an example, examination of the nuclear spin selection rule in chemical reactions will be discussed. Another important phenomenon in solid parahydrogen is the occurrence of tunneling chemical reactions. Tunneling effects become dominant at low temperatures in most reactions, but few studies have been reported due to the difficulty in observing reactions at low enough temperatures. We found that some radicals produced in solid parahydrogen induce tunneling reaction with a nearby hydrogen molecule. Details will be discussed.

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WKB Theory of Tunneling Splitting in Polyatomic Molecules

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There are basically three kinds of problems in tunneling: (i) energy splitting in a symmetric double well potential, (ii) tunneling decay through a potential barrier, and (iii) tunneling in reaction. Here we report a powerful general semiclassical theory for (i) and (ii) applicable to real polyatomic systems [1–2]. As for the demonstration of the theory, practical applications to real polyatomic molecules are reported [3–6]. High level of accurate quantum chemical *ab initio* computations are required in order to produce reliable results. Although these computations are very much time consuming, a practically feasible methodology has been established.

For the third problem mentioned above, the most important problem is how to detect the caustics efficiently in multi-dimensional systems. If time allows, a new efficient method is explained [7].

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Modeling spectra of fluorescent proteins with reference to low temperature experiments

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Photoactive proteins containing light-absorbing organic chromophores play a crucial role in living organisms. In particular, they include light converters which emit light as a consequence of the primary photoexcitation as in Green Fluorescent Protein (GFP) like proteins, widely used nowadays in biology and medicine as biomarkers in vivo. Modern spectroscopy tools are intensively used to gain the knowledge of events occurring upon photoexcitation of organic chromophores in various media, and low temperature experimental conditions are often helpful in assigning spectral properties of fluorescent proteins.

A newly discovered GFP-like protein from the sea anemone *Anemonia sulcata* asFP595 is initially nonfluorescent, but in response to intense light irradiation at 568 nm it becomes brightly fluorescent (kindles) with emission at 595 nm at room temperature. The mechanism of kindling is far from being clear, and presently substantial efforts are being undertaken to understand the intriguing properties of asFP595.

We apply *ab initio* type quantum mechanical – molecular mechanical (QM/MM) calculations to find equilibrium geometry configurations of large fractions of fluorescent proteins including the chromophore and surrounding residues. This QM/MM method is based on the effective fragment potential (EFP) theory, implemented in the GAMESS(US) and PC GAMESS program systems. This is an approach which allows one to perform calculations close to an *ab initio* treatment of the entire molecular system. In this scheme, molecular groups assigned to the MM part are represented by effective fragments which contribute their electrostatic potentials expanded up to octupoles to the quantum Hamiltonian. These one-electron electrostatic potentials are obtained in preliminary quantum chemical calculations by using *ab initio* electron densities. The exchange-repulsion potentials to be combined with the electrostatic terms can be also created in preliminary *ab initio* calculations. Thus, all empirical parameters are entirely contained in the MM subsystem.

At the QM/MM optimized geometry configurations of the kindling protein asFP595 the spectral parameters of the S_0-S_1 vertical transition of its chromophore in the protein matrix have been evaluated by using the time-dependent DFT method or *ab initio* CASSCF method. The results of simulations provide a theoretical support to the hypothesis on the possibility of *trans-cis* izomerization of the chromophore in the mechanism of kindling. The system can absorb light in the *trans* anion form of the chromophore and emit at longer wavelength in the *cis* anion form.

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Thermal and selective photochemical formation of noble-gas containing molecules and their host-guest interactions

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The family of HNgY–type molecules (Ng = Ar, Kr or Xe and Y = electronegative fragment) amounts nearly 20, including also some radicals. Their bonding contains both covalent and ionic contributions, and this is by now fairly well understood. Quite interestingly, after photodissociation of the HY precursor, the fragments can become separated, and thermal mobilization forms the HNgY product which process competes with direct formation of the molecule [1].

Special cases of the photochemical control of formation and decomposition will be discussed, HxeI [2] and HxeCC [3] being examples. Narrowband excitation of the v = 3 of the H-Xe stretching mode of HXeI decomposes the molecule into a local neutral atom configuration, which reacts upon thermal activation and also by tunnelling. Also, by narrowband IR –excitation HXeCC radicals decompose into a metastable H + XeC_2 configuration, and selective excitation of the vibrations of XeC_2 recovers HXeCC, this being an example of a selective and reversible control a chemical reaction.

The strong dipole moment of the HNgY species makes them excellent probes for intermolecular interactions. Based on synthesis between experimental and computational data, it seems that the HNgY molecules mainly interact with one host atom and such interaction often blueshifts the H-Ng stretching absorption [4–6].

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Matrix Isolation of Di- and Triradicals – New Design of High-Spin Molecules

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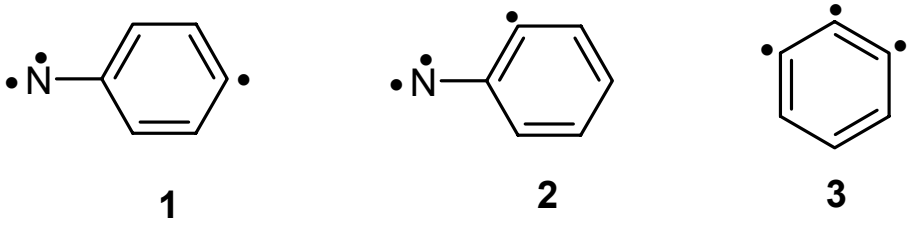
The interactions between the unpaired electrons in polyradicals leads to interesting systems with close lying high- and low-spin states. While a number of diradicals have been studied in detail by matrix isolation spectroscopy and other spectroscopic techniques, the investigation of triradicals with spectroscopic and theoretical tools is still in its infancy.

Here we describe the matrix isolation and spectroscopic characterization of dehydrophenylnitrenes **1** and **2** as prototypes of σ,π,σ-triradicals and 1,2,3-tridehydrobenzene **3** as a prototype of a σ,σ,σ-triradical.



1 **2** **3**

Dehydrophenylnitrenes **1** and **2** are interesting species which unite two motives of reactive molecules: phenylnitrene and phenyl radical. Depending on the position of the radical center relative to the nitrene moiety a high spin or a low spin system is predicted by *ab initio* calculations [1]. This is confirmed by EPR studies which demonstrate that derivatives of **1** and **2** exhibit unique spin systems with quartet ground states [2]. The 1,2,3-tridehydrobenzene, on the other hand, shows a low-spin doublet ground state [3].

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Diatomics in matrices: coherent control of the chromophor-lattice interaction

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Photochemistry in the condensed phase rests on a vibrational and/or electronic excitation of the chromophor molecules. The change in electronic wave function and in vibrational amplitude in going from the ground state to the excited state leads to an excitation dependent coupling to the environment. It is reflected for example in the line shape of the transition with pronounced sharp zero phonon lines in the weak coupling case and broad multiphonon continua vice versa. This coupling influences nonradiative vibrational and electronic relaxation rates, increases predissociation matrix elements and thus determines photochemical reaction pathways and efficiencies. We illustrate that the dynamics of these processes can be recorded in detail by femtosecond pump-probe spectroscopy [1]. The spectral bandwidth resulting from the pulse duration excites a bunch of vibrational levels coherently thus preparing the vibrational wavepackets required to resolve the dynamics. In this way the full spectrum of the phonon side bands contributes to the wavepacket dynamics [2]. Improving the experiments by applying a pair, or even more selective, sequences of coherent pulses with stable and variable relative electronic phase allows to excite with a spectral comb. The comb spacing can be adapted to the vibrational spacing and positioned via the phase on specific features of the line shape. We show that vibrational wave packets composed either of zero phonon lines or of a subset in the phonon side bands can be prepared in this way. These wavepackets follow different dynamics due to the variation in the coupling to the environment [3]. In addition the electronic and vibrational coherence times can be extracted. We show that these times exceed some ps for Br_2 and Cl_2 in rare gas matrices for a well chosen range of electronic and vibrational excitation energies. These times correspond to several vibrational periods and give room for a flexible application of these techniques.

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Thermal and photoinduced reactions in mesogenic matrices doped by d- and f-blok metals at cryogenic temperatures

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The systematic IR-, UV- and ESR-study of specific interactions and reactions of atoms and clusters of some d- and f-blok transition metals (Cu, Ag, Sm, Eu) were carried out for low temperature co-condensates of mesogenic cyanobiphenyls (CB) and cyanophenylpyridines (CPhPy) at 80-350K. Metal atom and small clusters containing mesogenic matrices of long-chain alkylcyanobiphenyls and alkylcyanophenylpyridines were obtained by reagent's and matrix components vapors co-condensation on the cooled surfaces of quartz, KBr or CaF_2 or polished copper under molecular beam conditions. IR, UV-Vis and ESR spectroscopic studies of the film samples were realized in situ, in vacuum, using special spectral cryostats.

The formation of metastable biligand complexes of metal atoms was shown during co-condensation process. Thermal and photodecomposition of the complexes at definite temperatures led to matrix controlled aggregation of metal atoms. The kinetics of complex thermal degradation and metal cluster's growth were studied by ESR technique. The interaction of metal atoms, clusters and nanosize particles, stabilized in mesogenic matrices at different temperatures with active was shown. The products of thermal and photoinduced reactions of metal species with chlor-containing compounds were analysed by UV-Vis and ESR techniques. Different relative reactivity of metal atoms and clusters was shown.

The formation of two sandwich complex structures with different stoichiometric metal to ligand ratios ML_2 and M_2L_2 was shown for Sm(Eu)/CB and Sm(Eu)/CPhPy systems by combination of spectral data with the results of DFT-B3LYP modeling of the system. The transformation of mononuclear lanthanide complex to the binuclear one was established at 80-350 K. ***Acknowledgements.*** The work was supported by RFBR grant 04-03-32748 and INTAS grant 2000-00-911.

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Cryomodification of solid drug substances

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Low and extra-low temperatures open the possibilities of detailed study of different chemical reactions, allow to carry out the unusual chemical interactions [1]. Recently low temperature techniques have been applied for producing and stabilization of nanoparticles of different chemical nature. At the moment the new research direction begins to develop – nanocryochemistry. In this presentation one of the possibilities of nanocryochemistry concerning of cryomodifiocation of drug substances is analyzed.

The chemical activity of solid organic drug substances and their biological activity strongly depend on their polymorphic modification, supramolecular organization and structural ordering, particle size and shape. These specific features determine biopharmaceutical and therapy activity of the drug forms. Production of structure and size-modified drug substances was realized via cryoformation of the solid phase substance by metastable state obtained by low temperature condensation of their vapors on the cooled surface. The samples of gabapentine (1-aminomethyl)cyclohexaneacetic acid, moxomidine 4-chloro-N-(4,5-dihydro-1H-imidazol-2-yl)-6-methoxy-2-methyl-5-pyrimidinamine, carvedilol 1-(9H-carbazol-4-yloxy)-3-[[2-(2-methoxyphenoxy)ethyl]amino]-2-propanol. The obtaining of drug substances structural modifications was realized using static and flow vacuum setups. Organic vapors condensation was carried out on polished copper cube or glass tube cooled by liquid nitrogen. Physical and chemical properties of cryomodified substances were studied by UV- and FTIR-spectroscopy, calorymetry. We controlled particle size and distribution by optical microscopy, scanning probe microscopy and their structure by X-ray diffraction. The composition of the former compounds and condensation products was controlled by chromatographic methods. On the example of gabapentin the formation of three different forms was established. One of them is not described previously in the literature, the size of particles obtained at 77 K was equal to 0,5 mkm. Particle size rises by increasing the condensation temperature. For moxomidine and carvedilol we have found also the minimization of particle size during cryoformation. The modified drug substances possess biological activity different from the former substances. Carvedilol has been obtained in amorphous state and shows high biological activity differs from the characteristic of commercial product.

The proposed method of cryomodification allowed us to carry out the micronization of drug substances by solvent free synthesis and obtained new physical, chemical and biological properties for know substances. *Acknowledgements.* The work was financially supported by Russian Foundation of Basic Research grant 05-03-32293.

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Low temperature chemistry in USSR and Russia

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The development of Low Temperature Chemistry in Russia and USSR is connected with the names and works of academicians N.N.Semenov, V.V.Voevodskii, V.I.Goldanskii, N.S.Enikolopov, S.S.Medvedev, V.A.Kargin, V.A.Kabanov, O.M.Nefgedov and many of their apprentices and followers.

The beginning of Low temperature Chemistry was established by the early work of N.N.Semenov (1928) on condensation of cadmium and sulfur vapors on surface cooled to 77 K. Systematic investigations on Low Temperature Chemistry rapidly developed in the middle of 50-th years and were connected with the search of possibilities to use highly energetic frozen radicals' condensates as a rocket propellant.

The most important influence on the development of Low Temperature Chemistry in USSR and Russia was caused by:

-obtaining, stabilization and reaction of atoms and radicals at low and extra low temperature, based on the application of light and X-ray radiation, matrix isolation and electron paramagnetic resonance methods;

-realization of chain induced by radiation and metal vapors polymerization processes in the solid sate;

-detection of fast, almost explosive processes of halogenations, hydro halogenations and nitration in the solid state at nitrogen and lower temperatures;

-discovery of low temperature limit of reaction rate on the examples of formaldehyde and other compounds;

-finding of avtowave (self-propagating wave) processes of cryochemical transformations, connecting with the existence of local stresses and mechanic-energetic chains;

-reactions of metal atoms, clusters and nanoparticles with organic and inorganic compounds, which transformed Low temperature Chemistry to Nanocryochemistry;

-combination of experimental research with the deep understanding mechanisms of cryoreactions on the base of theoretical models and representations, that is typical for Russian scientists.

In 1979 the First All-Union Conference on Low Temperature Chemistry took place in USSR, in Moscow State University, and in 1994 in Russian Federation was held the ***First International Conference on Low Temperature Chemistry.***

Chapter 2

Oral Presentations

High resolution ESR spectroscopy of FC_{60} and FC_{70} in solid argon: reassignment of the FC_{70} regioisomers

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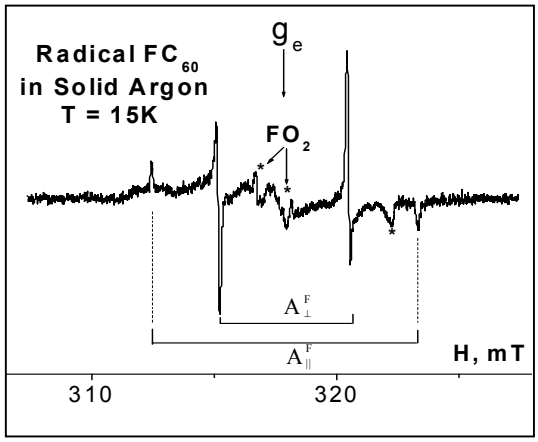
Solid argon films doped by fullerene molecules (C_{60} or C_{70}) and F_2 were prepared by thermal sublimation of the fullerite and co-deposition of the fullerene molecular flow and the gas mixture Ar/F_2 into cold (15 K) substrate. The stabilized free radicals FC_{60} (or FC_{70}) were generated in sold argon by means of chemical reaction of the photogenerated fluorine atoms with isolated fullerene molecules. High resolved anisotropic EPR spectra of the radicals FC_{60} and FC_{70} have been obtained for the first time in solid argon. The spectra of such species are characterized by axial-symmetric hyperfine interaction (hf) on ^{19}F nuclei. Performed quantum chemical calculations show that DFT method (B3LYP/L22) gives good agreement between the measured and calculated hf constants of FC_{60}: isotropic hf constant A_{iso}(expt.) = 202.8 MHz and magnetic dipole interaction constant A_{dip}(expt.) = 52.9 MHz.



Unlike C_{60} where only one monoadduct is obtained, atom addition to C_{70} can give rise to five isomeric FC_{70} adducts due to five distinct carbon atoms of C_{70} to which an atom can add (**A**, **B**, **C**, **D** and **E**). The obtained EPR spectrum shows that the reaction $F+C_{70}$ produces three regionisomers of FC_{70} in solid argon.

Comparison of the measured hf constants, A_{iso} and A_{dip}, with those obtained in calculation allows us to give the definite assignment of the spectra of the generated isomers, which strongly differs from previous description in ref.[1]. The conclusion is that the reaction of F atom with asymmetric double bond in C_{70}, like C_A-C_B and C_D-C_E, demonstrates strong selectivity producing only one regioisomer, **A** and **D**.

This work was supported by the Russian Foundation for Basic Research (Grant 04-03-32599) and Russian Academy of Sciences (Program OKh-01).

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Supramolecular photochemistry of van der Waals complexes of molecular oxygen

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In the current work the effect of weakly bound partner X on molecular oxygen O_2 photoabsorption and photodissociation is experimentally studied on the model system which is van der Waals (vdW) complex of the type X-O_2 where X is molecular or atomic partner. This model is used to study the partner X effect on photoabsorption and photodissociation of oxygen in cryogenic matrix, solution of O_2 in liquids or "collisional" complexes X-O_2 in gas phase. The experimental approach involves the photoexcitation of vdW complex X-O_2 with the polarized laser radiation with quantum $h\nu$ exceeding the threshold for dissociation of molecular oxygen $O_2 \xrightarrow{h\nu} 2O(^3P_j)$ and then the probing the yield, kinetic energy and angular distribution of the photofragments. The vdW complexes generated in the pulsed molecular beam were excited within Herzberg continuum by UV-laser. This UV radiation was tuned to the 2-quantum resonance of $O(^3P_j)$ atoms at ≈226 nm to provide simultaneously the ionization of O photofragments via (2+1) REMPI. The dramatic raise of the cross-section of O atoms photogeneration in vdW complexes as compared with the isolated O_2 molecule has been observed. The angular anisotropy of O-atom recoil directions and velocity distribution have been measured with the use of velocity map imaging technique (Eppink and Parker, Rev. Sci. Instrum. **68**, 3477 (1997)). In Figure 1 the velocity map image of $O(^3P_2)$ atoms arising in the photodissociation of the free O_2 molecule and complex CH_3I-O_2 is presented.

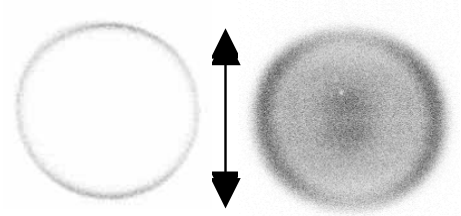

Fig. 1. The sliced velocity map image of $O(^3P_2)$ atoms arising from left) - the dissociation of the free O_2 molecule and right) - van der Waals complex CH_3I-O_2. The direction of electric field vector of exciting radiation is shown by double sided arrow. The radius of the ring is proportional to velocity of O atoms.

These images demonstrate the drastic change of the mechanism of O atom photogeneration from complex as compared with the free O_2 molecule. Several modes differing by kinetic energy and angular anisotropy of O atoms correspond to several microscopic channels of O atoms appearance from excited van der Waals complex CH_3I-O_2. Similar results have been also obtained for several other van der Waals complexes of the type X-O_2 with atomic and molecular partners X. The production of O atoms from vdW complex X-O_2 is established to be governed by contribution of two excited states of the complex: 1)-the supramolecular charge-transfer state of the complex X^+-O_2^- and 2)-states with excitation localized on O_2 molecule in complex. The results obtained have allowed us also to deduce the mechanism of symmetry breaking by complex partner X resulting in the O_2 "absorption enhancement". The effect of the nature of X species on the photoprocesses in vdW complex X-O_2 has been analyzed.

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Cryoformation and electrophysical properties of metal and semiconductor nanosystems

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Gas sensorics is one of the possible applications of nanochemistry. In order to produce nanomaterials for gas sensors one has to control their microstructure and properties. There are many different methods for preparation of nanomaterials [1]. Among the promising synthetic approaches there is a Low-Temperature Physical Vapor Deposition (LTPVD) technique. It is based on deposition of vapors on cold substrates followed by controlled annealing.

In this work the LTPVD has been used to produce nanostructured metal, semiconductor and metal-semiconductor films. Thus we synthesized and studied the condensates of Pb, PbS, and hybrid structures of Pb/PbS and Pb/PbO.

We found that the deposition of Pb on Al_2O_3 at 80 K up to percolation threshold followed by annealing to 300 K results in formation of thin films with fractal-like microstructure. The mean particle size was found to be around 50 nm. Surprisingly, the percolation threshold and microstructure of the film after annealing depended on preparation conditions, namely the deposition flux [2].

To study the observed effects at the atomistic level, the early stages of Pb film growth at different deposition conditions were simulated using the combination of classical Molecular Dynamics and Temperature-Accelerated Dynamics.

In order to cover the metallic particles by semiconductor shells the samples were exposed to oxygen and hydrogen sulfide. Besides, the films of individual lead sulfide were prepared by PbS deposition. To modify the structure of Pb films the low-temperature codeposition of lead with carbon dioxide was carried out.

Electrophysical properties of prepared samples were studied after annealing using Keithley 6517A electrometer in air with different humidity and ammonia concentrations. It was found that the samples are sensitive to relative humidity in range 40–100 %.

Thus, the LTPVD can be used to produce nanostructured thin films and manage the microstructure and chemical content of the film particles for gas sensor applications. The combination of Molecular Dynamics with Temperature-Accelerated Dynamics can be used to obtain the information about the atomistic processes, occurring during LTPVD.

The work was partially supported by RFBR grant #05-03-32293.

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Solvation of excess electrons in superfluid ^{4}He

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An efficient numerical method, based on the imaginary time propagation of Schrödinger equation (ITP), was developed for solving large-scale matrix eigenproblems [1]. When the ITP method was combined with the fourth order operator splitting technique and our new dynamic time step adjustment procedure, the computational scaling as a function of the matrix size was much better than have been observed for Lanczos based algorithms. Using this method, we were able to carry out calculations to model the solvation of both singly and doubly occupied electron bubbles in superfluid [4] He without any geometry restrictions (i.e. in 3–D). For example, it was now possible to model the anisotropic liquid localization around non-spherically symmetric electronic states. The applied theory is a combination of boson and fermion density functional theories [2], which are coupled by the electron – helium pseudopotential [3–5]. Formally, this model consists of two coupled non-linear Schrödinger equations. In the case of single electron bubbles, our interests are mainly in obtaining the static solvation structures for the electronically excited states and to understand the related optical absorption and emission spectroscopy. For doubly occupied electron bubbles, the most important questions are their possible existence and spectroscopic detection [6]. Results from both density functional theory and configuration interaction calculations are discussed.

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Laser Flash Photolysis of Phenanthroline-containing Spirooxazines in a Frozen Methanol Matrix

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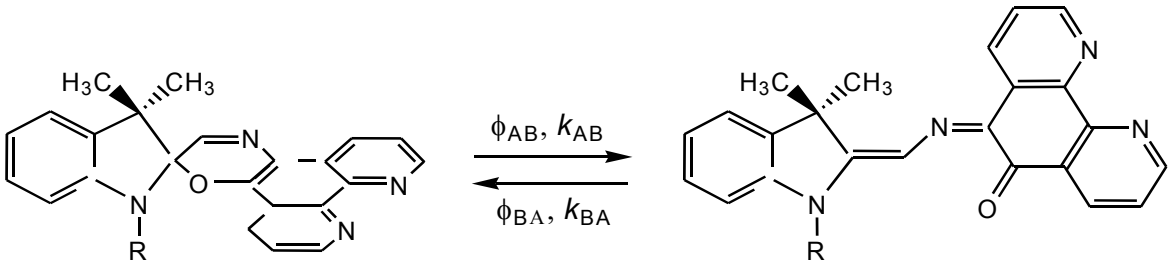
Both stationary and laser flash photolysis were applied to study the photochemistry of a closed A-form of phenanthroline-containing spirooxazines in a methanol matrix (77 K). One of spirooxazines was nonsubstituted (SPO1) and the second one (SPO2) had a long alkyl substituent, n-$C_{16}H_{33}$, in the indoline part of the molecule (Fig. 1). For SPO1, excitation of the A-form causes the appearance of the B-form absorption (600 nm) during the action of a laser pulse. Kinetics of a further increase in the concentration of B-form is determined by the inhomogeneity of a rigid matrix and is described by a set of exponents with characteristic times from hundreds of nanoseconds to tens of milliseconds. Absorption of the B-form is accompanied by absorption in the region of 400 – 750 nm, which belongs to X-isomer (an intermediate form of spirooxazine).



A **B**

Figure 1. Closed A spiro-form and open merocyanine B-form of spirooxazines SPO1 (R ≡ CH_3) and SPO2 (R ≡ n-$C_{16}H_{33}$).

The disappearance of X-isomer was described by a set of exponential functions with the characteristic times similar to those typical of the B-form appearance. For SPO1, only the B-form is accumulated during the stationary photolysis (X-isomer is completely transformed into the B-form). For SPO 2, a range of characteristic times moves toward long times so that the X-isomer absorption is observed even upon stationary photolysis. Thus, a long X-isomer lifetime indicates that the B-form originates from the ground state of this intermediate. The existence of a long substituent substantially increases the time of X → B transformation in a frozen matrix. The appearance of a narrow absorption band at 600 nm immediately after the laser pulse was assigned to the formation of only one of the possible isomers of B-form upon X → B transformation.

The work was supported by the Russian Foundation of Basic Research (grant No. 05-03-32268) and the Program of Integration Projects of Siberian Branch of Russian Academy of Sciences (grant No. 77).

Simultaneous transitions in liquid nitrogen solutions: Theory and Experiment

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Among the variants of electric dipole transitions induced during intermolecular interactions are the so-called simultaneous transitions, in which the absorption of one photon leads to the simultaneous excitation of both interacting molecules. In the electrostatic mechanism of induction, the probabilities of simultaneous vibrational transitions are dependent in a well-known manner on the electro-optical parameters of the molecules and on the intermolecular interaction potential.

Thus far, the great majority of publications have dealt with the study of induced interactions of spectra of gases. Induced spectra of condensed systems have been studied much less; in particular, there are almost no data on the probabilities of simultaneous transitions in the condensed phase.

To fill the gap, we have initiated an experimental and theoretical study of the simultaneous transitions in solutions of simple solute molecules such as NF_3, CF_4, SiF_4, SF_6 and CF_3Br dissolved in liquid nitrogen and in liquid argon / liquid nitrogen mixtures. For all simultaneous transitions observed, the probability is determined by determining the intensity ratio of the simultaneous transition $\nu^x_{solute}+\nu_{N_2}$ with respect to that of the fundamental ν^x_{solute}. The experimental data are compared with theoretical values obtained by combining Monte Carlo simulations and anharmonic force field calculations in which the mechanical and the electric anharmonicities are taken into account explicitly.

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The Peculiarities of Radiation-Initiated Copolymerization at Low Temperature

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If copolymerization proceeds in liquid phase, the composition of copolymer is determined by the reciprocal reaction ability of co-monomers. As far as an active monomer is spent, the resulted copolymer is almost always enriched by less active monomer and polymer chains have an inhomogeneous composition. If the reaction it initiated using the radiation-chemical method, active radiation centres are accumulated, and the whole process can be conducted in solid or viscous overcooled state at significantly lower temperatures then with the use of chemical initiators. These specific reaction conditions proceedings in significant increase of reagent contact time, lead to essential changes in idea of co-monomer reaction abilities.

Matters examined in the report: 1) autowave regimes of cryopolymerization, initiated by the local indignation (brittle fracture) of solid samples that were pre-irradiated at 77 K; 2) cryopolymerization of dienes (butadiene, isoprene, etc.) and α-olefines with sulphur dioxide; 3) low-temperature copolymerization of some monomers (N-vynilpirrolidone, divinyl sulfone, acrylamide, acrylic acid, methylacrylate) in viscous overcooled liquid after devitrification of glassy systems that were pre-irradiated by γ-rays at 77 K; 4) kinetic peculiarities of low temperature processes of copolymerization forestalled by irradiation. The formation mechanism and conditions for creation of the statistical (when composition corresponds to compound of initial mixture) and alternate copolymers were found. It was shown that it is possible to form homogeneous copolymers and to manage their composition. The phase state of system takes effect on composition of copolymer and on dynamic of post-irradiation copolymerization. It was shown that if one of comonomers is in excess in copolymerization of isoprene with SO_2 (the typical pair of monomers for alternate copolymerization in standard conditions), then order of alternating elements in co-polymer may be broken. The kinetic model that an account the peculiarities of low-temperature post-irradiation copolymerization and well conforms to experimental data was suggested. Using the autowave copolymerization regime, the copolymers were created at the temperature close to absolute zero. The creation of copolymers at such a low temperature may have a value for understanding of cold chemical evolution of compounds in the Universe.

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Structural Studies of Nanoclusters in Impurity-Helium Condensates

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Impurity-helium condensates are highly porous gel-like materials consisting of interconnected clusters of various atomic and molecular species immersed in liquid helium. The characteristic cluster size is 3-10 nm, and the clusters can be made of noble gases, hydrogen, nitrogen, water, and of a number of other compounds. Extremely large concentrations of free radicals can be stabilized in these systems, and impurity-helium condensates have been successfully used for investigations of several fundamental low-temperature tunneling exchange reactions. Herein, we report structural studies of Ne, Ar, and Kr impurity-helium condensates. Our synchrotron x-ray diffraction measurements demonstrate that the impurity clusters in the condensates are multiply twinned particles with five-fold symmetry. Specifically, the smallest clusters can be described as modified icosahedra, while decahedral clusters appear in the condensates with a larger average cluster size. These results provide evidence that the condensates consist of weakly interacting, or even individual, impurity nanoclusters that are prevented from the coalescence by thin layers of adsorbed helium. Therefore, impurity-helium condensates hold promise as a new medium for cluster physics studies, as well as for matrix isolation spectroscopy, and studies of low-temperature chemical reactions.

Spectral Detection of Unstable 6-coordinate Species Containing Nitrogen Oxides Complexes of Heme models

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Nitrogen monoxide (NO), nitrite (NO_2^-) and nitrate (NO_3^-) are metabolically linked oxides of nitrogen that take part in a number of biological processes in living systems. For this reason nitrogen oxides' complexes of heme models are a continuing focus of attention.

In this presentation we report the use of sublimed layers methodology [1] to investigate a number of previously unknown 6-coordinate nitrogen oxides' adducts of heme-model iron-porphyrins Fe(Por), (Por = TPP and TTP are meso-tetraphenyl- and meso-tetra-p-tolyl-porphyrinato dianions correspondingly). These were stabilized at low temperature conditions and detected by FTIR and UV-visible spectroscopy. Examples are listed below.

- Interaction of iron-nitrosyls Fe(Por)(NO) with excess of trimethylphosphine {$P(CH_3)_3$, TMP} at low-temperature conditions leads to formation of (TMP)Fe(Por)(NO) that results mostly in Fe(Por)$(TMP)_2$ upon warming.
- Low-temperature interaction of recently discovered Fe(Por)(η^1-ONO) [2] with NO or TMP ligands results correspondingly in the formation of 6-coordinate nitrito species (NO)Fe(Por)(η^1-ONO) and (TMP)Fe(Por)(η^1-ONO) that isomerize to nitro complexes (NO)Fe(Por)(NO_2) and (TMP)Fe(Por)(NO_2) upon warming.
- Interaction of NH_3 with iron porphyrin nitrato complexes Fe(Por)(η^2-O_2NO) at low temperatures leads to displacement of nitrato anion and formation of the 6-coordinate ammonia complexes [Fe(III)(Por)$(NH_3)_2$][NO_3^-]. This process is reversible and upon warming ammonia complexes decompose restoring initial nitrato-complexes Fe(Por)(η^2-O_2NO).
- Interaction of tetrahydrofuran (THF) with bidentate nitrato-complexes Fe(Por)(η^2-O_2NO) leads to formation of thermally unstable nitrato complexes (THF)Fe(Por)(η^1-ONO_2). As in the case of previously observed nitrato-nitrosyl complex [3] coordination of a ligand in the *trans* axial position leads to isomerization of the bidentate nitrato ligand to the monodentate complex (THF)Fe(Por)(η^1-ONO_2).

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Low-Temperature IR and Quantum-Chemical Studies of Complexation of Metallocenes with Molecular Nitrogen

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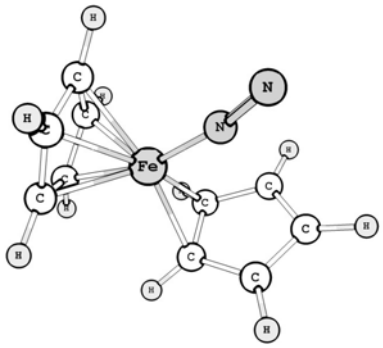
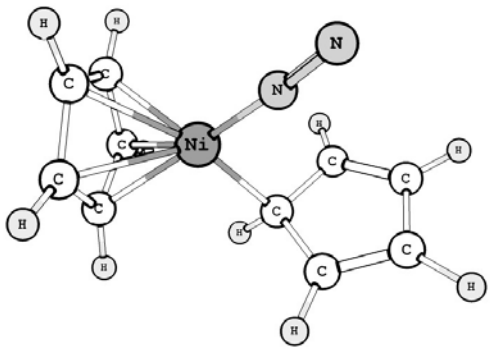
Earlier we found by low-temperature IR spectroscopy that co-deposition of dinitrogen and metallocene Cp_2M ($Cp = \eta^5$-C_5H_5, M = Fe, Co, Ni, Mn, V) from the gaseous phase to a support cooled to 12-20K resulted in complexation of Cp_2M with N_2 [1]. This was confirmed by the appearance of absorption near 2140 cm^{-1} associated with N_2 stretching vibrations and 200 cm^{-1} low-shifted as compared to absorption of free N_2 molecule. Nitrogen coordinates to a metal atom in the monodentate fashion, which was proved by experiments with the mixed $^{14}N^{15}N$ isotope. In these experiments, two ν(NN) bands were observed for complexes M-$^{14}N^{15}N$ and M-$^{15}N^{14}N$ differing in 6 cm^{-1}, being in agreement with predicted values.

Up to now the structure of compounds obtained has not been clear. In this work the structures of these complexes was calculated by the DFT method. At the first stage the applicability of the DFT method to calculation of vibrational spectra of initial organometallic compounds (where) was investigated. The calculations were carried out using Gaussian98 and Gaussian03 program packages with BLYP, B3LYP, and SDD functioanals in LanL2DZ, 6-31G*, 6-31G**, 6-31+G(d,p), 6-31G(3df,3dp), 6-31++G(3df,3dp), 6-311G basis sets, as well as using PRIRODA program package developed by D. N. Laikov [2] with the PBE functional in the 3z, sbk, and mixed basis sets. The PRIRODA program was used for calculations of complexes with N_2. Calculations with PRIRODA program gives practically the same results with all three basis sets, but calculations run faster and the results are markedly better that with Gaussian program.



νNN=2109 см$^{-1}$



νNN = 2182 см$^{-1}$

Calculation show that complexes of metallocenes with dinitrogen do exist, the Cp rings in these complexes deviate from being parallel, one ring maintains the η^5 coordination, but the bonding of the other ring is closer to the η^2 or η^1 type (see the Chart). The calculated shifts of ν(NN) frequencies compared to that for free N_2 molecule (2359 cm^{-1}) are 165 and 239 cm^{-1} for complexes Cp_2Ni and Cp_2Fe, respectively.

This work was supported by RFBR (grant 04-03-33117) and by the program of the Division of Chemistry and Material Sciences of RAS.

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Theoretical Study of the Reactivity of 1st Row Transition Metal Atoms with CO_2, CS_2, and OCS

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The calculation of potential energy surfaces of the reactions of Sc, Ti, V, Fe, Ni, and Cu ground state atoms with CO_2, CS_2 and OCS molecules has been performed by means of density functional method at the B3LYP level with the overall energetic being refined at the CCSD(T) level.

For the lowest energy routes, we have shown that:

- among the three molecules, the CS bond of OCS is always the most reactive one,
- metals from the left side of periodic table undergo insertion reactions without energy barrier, whereas metals from the right side lead to insertion products via the formation of intermediate coordination complexes which lie below the energy level of reactants.

When available, comparisons are made with results obtained through low temperature matrix isolation spectroscopy and gas phase experiments.

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Various types of hydrogen bonding in simple hydroxamic acids and oximes complexes in cryogenic matrixes

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The ability of the COH group to act as a proton donor or a proton acceptor in hydrogen bonded complexes have been very extensively studied and its behavior in different types of hydrogen bonds is well known. On the contrary, the properties of the NOH group in the hydrogen bonded systems are far less recognized. Hydroxamic acids and oximes belong to important class of compounds that involve the NOH functional group; hydroxamic acids involve also the fragment of the simplest protein structure, namely HNC=O grouping. The interest in the properties of hydroxamic acids is stimulated by their biological activity, in turn many oximes are commonly used as pesticides and drugs. The properties of these two groups of compounds are effected by their ability to form various types of hydrogen bonding.

This work presents results on some interesting types of hydrogen bonds formed by simple hydroxamic acids and oximes. In particular the following issues will be addressed:

- formation of improper N-H···OC and NO-H···N_2 hydrogen bonds in the formohydroxmic acid complexes with CO and N_2;
- noncooperativity of the hydrogen bonds formed by the NH and NOH groups in formohydroxamic acid complexes with CO;
- hydrogen bonding in formohydroxamic acid and formaldoxime complexes with water and ammonia; the kinetic control of complex formation in formohydroxamic acid complexes;
- the cyclic six-membered dimers of formaldoxime;
- dimerization of the keto tautomer of acetohydroxamic acid.

The studies of the complexes have been performed in argon matrixes by help of FTIR spectroscopy. The experimental results have been supported by theoretical calculations. The energies and the spectra of the complexes were calculated at the MP2 level of theory using 6-311++G(2d,2p) basis set. The comparison of the theoretical results with the experimental spectra allowed us to support the spectroscopic characterization and explain some of the "experimental mysteries".

Characterisation and Reactions of Molecular Cesium Azide

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Matrix isolation infrared studies have recently been carried out on the vaporisation of several alkali metal azides, and the results show that under high vacuum conditions *molecular* CsN_3 can be produced as a stable high temperature vapor species. The characterisation of this novel molecule is based primarily on the spectroscopic evidence available from N-15 isotope studies, and is supported by *ab initio* molecular orbital calculations and DFT calculations [1, 2].

Subsequent experiments involving the nitrogen matrix *co-condensation* of molecular CsN_3 with a variety of substrates XY, where X is a halogen (Cl, Br or I), and Y is a second halogen or pseudo-halogen, have demonstrated that chemical reaction can take place during and after co-condensation in which novel azide species YN_3 are formed. These species are characterised by new ir features in the N_3 stretching region, and their identity is explored with the aid of pathway calculations for the systems $CsN_3 + XY \rightarrow CsX + YN_3$ together with DFT modelling of the vibrational spectra of possible products.

This presentation includes an interpretation of the most recent experimental and theoretical results on these novel systems.

Acknowledgement: We gratefully acknowledge the financial support of Qinetiq Ltd (UK) for part of this work.

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Femtosecond-CARS polarization beat spectroscopy of I_2-Xe in solid krypton

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Femtosecond coherent anti-Stokes Raman scattering (fs-CARS) can be used to investigate molecular coherences in condensed phase. The method includes the elements of preparation, manipulation, and interrogation of coherences, which is achieved by controlling the light pulse characteristics and timing between the pulses. In particular, the method can be used to study vibrational dynamics on the electronic ground state as has been shown in several studies of matrix isolated iodine [1-5].

In this work we have applied the fs-CARS method to study interaction between xenon and I_2 in solid krypton matrices. The polarizations induced in ”free” and complexed I_2 in the same sample lead to intermolecular interference and appearance of polarization beats in the time-domain signal [6]. When the concentration of complexed iodine is much smaller than that of ”free” iodine, the quantum beat signal from the complex is weak and difficult to detect. However, the complex signal is ”amplified” in polarization beats by the large amplitude polarization of the ”free” iodine, analogously to heterodyne detection. In addition, in Fourier transform of the time-domain signal, the peaks due to polarization beats are better separated from the ”free” iodine peaks than the ”pure” complex peaks. These experimental findings are confirmed by reproducing the signals by wavepacket simulations. Thus, it is shown in this work that polarization beat spectroscopy is a useful tool in studying molecular complexes. This is emphasized by experimental determination of accurate molecular constants for dilute I_2-Xe in solid krypton although the harmonic frequency differs from ”free” I_2 by less than 1 cm^{-1}.

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On theory of non-arrhenius autowave mechanisms of fast chemical evolution of matter in universe

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The work proposes new approaches for explanation of a many-centuries mystery concerning of nature of super-fast chemical solid state evolution of matter in the Universe under temperatures near to absolute zero and also chemical mechanisms of forming of the solid crust on the cold planets of the Solar system.

The concept is based on discovered two decades ago non-usual autowave self-propagation phenomena of anomalous fast transformations in the cryo-chemical reactions[1-2]. These travelling waves had velocities equal to ones in most fast high temperature processes of combustion nevertheless the transformations were realised under temperatures 4-77 K (in liquid helium and nitrogen). The chemical solid state waves initiated by local brittle fracture propagated layer by layer over the frozen sample of reagents . The chemical reaction starts on the surface resulting from local brittle fracture of the solid matrix. Temperature gradients arising during the reaction lead to further dispersion of the reacting sample. This feedback mechanism leads to propagation of autowaves of chemical conversion. Such an autowave regime is observed for several classes of reactions (hydrocarbon chlorinating, olefin hydrobrominating, polymerization and copolymerization). The classical Arhenius concept could not explain the phenomenon. These observations lead to a completely new autowave concept of chemical activity in solid state.

The developed theory of the phenomenon rests on the assumption that a mechanical energy accumulated in solid matrix can be transformed into a chemical energy even at extremely low temperatures, therefore leading to rates of chemical transformation many orders of magnitude larger than predicted by classical Arrhenius factors. This energy transformation is a result of self-sustained brittle disruption (dispersion) of solid matrix and this phenomenon may be named “autowave self-sustained tribo-chemical mechanism”.

The first simple theoretical model of autowave processes in solid-phase cryochemical reactions was proposed in [1-2]. The model considered was constructed on the physical scheme that brittle fracture is induced by thermal strain from reaction heat generation. The theory is being developed by the work [3] which are investigating different bifurcation phenomena concerning of critical conditions with parameters of heat-transfer, sample sizes, and also with thresholds of “cold” ignition of autowave transformation in frozen reagents by local disruption etc.

We suppose the autowave hypothesis may give an ideological base of fast cryochemical evolution of the cosmic substances. In particular, one can imagine the formation, from the frozen mixture of elements, of compounds such as ammonia and methane that are found in appreciable amounts in crusts of the cold planets of the Solar system.

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Intramolecular Hydrogen Bonding and Conformer's Structures of Nucleosides and Aminoacids in Rare Gas Matrices

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The intramolecular interactions mediated by H-bonding in single bioorganic molecules have been investigated. We present here matrix FTIR spectra of nucleosides, sugars, aminoacids and several active biological compounds isolated in argon, neon and krypton.

The experimental setup was developed for evaporating and trapping of thermounstable compounds in low temperature matrices. The low temperature differential quartz crystal microbalance was used for the measurements of absolute intensity of molecular beams of bioorganic compounds and rare gases. The evaporation cell is characterized by a working pressure of vapour around 10^{-5} Torr. The temperature range of cryogenic block is 5-25 K, FTIR spectra were obtained in the range 200 – 4000 cm^{-1}. *Ab initio* calculations of infrared spectra were performed by methods HF/3 – 21G(p) and 6-31G(d,p).

A-H and B groups exist in bioorganic compounds, and these groups results in H-bonding if geometric arrangement is favorable. Our recent results obtained by matrix-isolation infrared spectroscopy are following:

- It was shown that syn-conformations of uridine and thymidine are stabilized by intramolecular H-bond O5'H----O_2 whereas syn-conformation of adenosine have been stabilized by intramolecular H-bond of O5'H----N_3 type. The substitution of natural sugar by cyclic hydrocarbon decreases the concentration of minor conformers.
- The conformations of glucose, ribose and 2-deoxyribose are stabilized by intramolecular H-bonds. Some spectral bands of ribose and 2-deoxyribose in range $\nu(OH) \approx$ 3490 – 3520 cm^{-1} have been assigned to intramolecular H-bonding in different axial conformations.
- The forming of strong H-bond in 2-nitroresorcinol (it is a model compound for a proton pump) leads to considerable frequency shift of OH vibration when $\Delta\nu(OH)$ is about 400 cm^{-1}.
- Intramolecular H-bonds of NH_2…O=C, NH…OH and NH_2…OH types were identified in conformers of aminoacid glycine which were frozen in Kr, Ar or Ne matrices. Relative concentration of conformers was varied by UV irradiation, it was depended on matrix cage.

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Theoretical study of the structure and stability of new Xe-containing molecules with transition metal atoms

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Discovery of unusual XeH_2 species in low temperature rare gas matrices put on the question about stability of new class of Xe-containing molecules, which are different from well known case of HXeX molecules, where X is strong electrophile. Using quantum chemistry methods stability and structure of homoleptic Xe-containing molecules XeM_2 and MXe_n with transition metal atoms was studied. The stability of XeM_2 molecules is determined by the two factors. The first one is the energy of ionic dissociation of XeM_2 on M^+ , Xe and M^-, ΔE. The second factor is an equilibrium Xe-M distance R in XeM_2 molecule, which governs polarization energy of Xe atom in the electric field of neighbour ions. It can be estimated as

$$\approx \frac{1}{2}\left(\frac{2}{R^2}\right)^2 \alpha = \frac{2\alpha}{R^4}$$

If the relation

$$\Delta E > \frac{1}{R} + \frac{2\alpha}{R^4}$$

is fulfilled one could expect rather strong Xe-M coupling for the ground state of XeM_2 molecule, otherwise quasichemical M-Xe ineraction is possible but in metastable state only, which is located above the ground weakly bound van der Waals state.

In the case of strong coupling, due to ionic states $M^+|Xe|M^-$ and $M^-|Xe|M^+$ contribution in the wave function of XeM_2 molecule its dissociation energy is much larger then dissociation energy of van der Waals molecule XeM. In some cases the ratio of $D(XeM_2)/ D(XeM)$ achieves the value about 10. By the same reason the R value is much less then equilibrium distance for van der Waals molecule XeM.

Electronic structure calculations were carried out by nonempirical PBE density functional method using SBK pseudopotential with extended basis set and by many body perturbation theory MP2 and CCSD(T) using Stuttgart SDD basis set. These approaches are well enough to reproduce the known data about Xe-containing molecules.

It is interesting that Pd and Pt atoms have rather strong affinity to Xe atom. Corresponding dissociation energies for singlet molecules are: PdXe - 441 meV (PBE/SBK), 272 meV (CCSD(T)/SDD); PtXe - 473 meV (PBE/SBK), 692 meV (MP2/SDD). For Pt atom this value is larger then singlet-triplet splitting. For triatomic singlet molecules with Pd and Pt their binding energies can achieve the value of about 1 eV: PdXePd - 942 meV (PBE/SBK), 643 meV (CCSD(T)/SDD); XePtXe - 1357 meV (PBE/SBK), 1509 meV (CCSD(T)/SDD). XeM_2, M=Pd,Pt, molecules are not inert in Xe-matrix due to further M-Xe coupling with surroundings. For more simple case, investigation of the structures of $PdXe_n$ and $PtXe_n$, $n\leq 6$, shows the effect of saturation of binding energy with respect of number of Xe atoms. However it is hard to observe the molecules $PdXe_n$ and $PtXe_n$ in Xe-matrix using IR spectroscopy method for the reason of low vibration frequencies, lower than 200 cm^{-1} or about it. Probably optical absorption methods are much more appropriate for detecting these new species.

Structure, low-temperature transformations and catalytic activity of labile aluminum chloride complexes

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The Lewis acids are used as catalysts of the most important technological processes (alkane isomerization, arene alkylation, olefine olygomerization etc). The establishment of detailed mechanism of reactions with the Lewis acids is hindered by the difficulty of registration of active intermediates and unstable molecular complexes which are contained in very low concentrations at the conditions of chemical reactions. This work demonstrates the possibilities of low-temperature spectroscopy (IR, UV-) to study the catalytic complexes and intermediates, their dynamics and reaction mechanisms in the solid state taking aluminium halide complexes as an example of high active catalysts.

Using the low temperature condensation method the syntheses of aluminum chloride complexes with different promoters of catalytic activity (water, transition metal chloride, alkyl halide, nitroalkane) have been carried out in hydrocarbon matrices. Species of the various compositions were obtained; unknown earlier spectral characteristics (IR, UV/vis) and the regions of their thermal stability were revealed at 80-290K. The structures of the observable labile particles were proposed on the basis of the vibrational spectra and quantum-mechanical accounts with use of density functional theory.

Dynamic low-temperature studies *in situ* of multi-component systems allowed observing competitive activity of the reagents in the formation of labile complexes and intermediates and establishing the factors determining the direction of their transformations. For example, co-condensation (80 - 120K) of threefold system 2-chlorobutane-$AlCl_3$-$CoCl_2$ didn't result in formation of secondary butyl cation as it was observed in binary 2-chlorobutane-$AlCl_3$ system [1]. Only molecular triple complexes with cobalt coordination were observed in IR spectra. They were steady up to 240K, which their transformation in the ionic species followed, and a tertiary butyl cation was registered.

Depending on conditions at least 4 different complexes between aluminum chloride and cobalt halide were formed, in which the coordination number of cobalt was varying from 3 up to 6 [2]. The complexes of structure 1:1 and 2:1 were only precursors of the real catalyst; the active particles were forming only at interaction of different complexes. Reductions of absorption bands of initial complexes occurred at temperatures 120-150 K and the absorption bands of a new adducts grew. These intermediates represented the ionic species containing atom cobalt simultaneously in cation and anion parts, their formation was correlated with accumulation of products of alkane isomerization.

Linear and branched alkanes were activated by promoted aluminum chloride at low temperatures. The nontrivial way of alkane transformation resulting to creation a normal

alkane with smaller per unit of carbon chain was detected. Two mechanisms of promoting action by the transition metal salts and alkyl halides on the catalytic activity of aluminum halides were suggested. The composition and structure of aluminum chloride complexes was demonstrated to determine the route of the low-temperature alkane transformations.

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Theoretical study on chemical dynamics of helium clusters

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Impurity-doped helium clusters have recently attracted widespread attention from an experimental point of view because of their highly quantum-mechanical properties such as large zero-point motions, tunneling, and superfluidity. Due to recent advances in a molecular beam technique, as well as a laser spectroscopic technique, extensive studies have been performed using helium nanodroplet isolation (HENDI) spectroscopy so far, and those studies have given new insight into the unique quantum nature of atoms and molecules embedded in helium clusters [1]. Motivated by this experimental advance, our group has recently started a research project to study the dynamical processes of atoms and molecules embedded in helium cluster from a theoretical point of view.

As a new simulation tool for handling quantum dynamics of the solute in the presence of quantum solvent, we have recently developed a hybrid simulation scheme in which the time-dependent quantum dynamics method is used for the solute motions while the semiclassical path integral centroid molecular dynamics method is employed for the solvent motions [2]. The centroid molecular dynamics method has originally been developed by Voth's group. In this method, the quantum fluctuation of a quantum particle is represented by cyclic imaginary-time path conformations called ''beads'' and the centroid, which is defined as the center of mass of these beads, is then propagated by the equations of motion.

We have applied this newly developed method to the photodissociation of Cl_2 in a helium cluster [3], electronically nonadiabatic photoexcitation dynamics of the silver atom in a helium cluster [4], and K*He_n exciplex formation dynamics on a helium cluster [5]. All these simulations show the importance of the quantum nature of helium motions. Details of our calculations will be presented.

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Theoretical study of chemical binding of transition metal complex with noble gas atom

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Ab initio multireference and coupled cluster methods (MR-SDCI(+Q), CASPT2, CCSD(T)) and density functional theory methods (B3LYP, MPWPW91) have been applied to examine geometrical structures and vibrational frequencies of noble gas (Ng) – transition metal compounds, Ng-NiCO, Ng-NiN_2, and Ng-CoCO (Ng = He, Ne, Ar, Kr, Xe) [1,2,3]. By including the zero-point vibrational energy and the counterpoise correction, the binding energy was evaluated as 6.63 kcal/mol (Ar-NiCO), 8.53 kcal/mol (Ar-NiN_2), and 5.11 kcal/mol (Ar-CoCO) at the MPWPW91 level. The binding mechanism is explained by a partial electron transfer from a noble gas atom to the low-lying 4s and 3d vacant orbitals of the transition metal atom. Theoretical calculations show that the binding of noble gas atom results in a large shift of the bending frequency: 361.1 cm^{-1} (NiCO) to 403.5 cm^{-1} (Ar-NiCO); 308.5 cm^{-1} (NiN_2) to 354.8 cm^{-1} (Ar-NiN_2); 373.0 cm^{-1} (CoCO) to 422.6 cm^{-1} (Ar-CoCO). The corresponding experimental frequencies determined in solid argon are 409.1 cm^{-1} (NiCO), 357.0 cm^{-1} (NiN_2), and 424.9 cm^{-1} (CoCO) [4,5,6], which are much closer to the corresponding frequency of Ar-NiCO, Ar-NiN_2, and Ar-CoCO, respectively. The intensity and isotopic shifts for several isotopomers also show that the experimental values are much closer to those calculated ones of Ar-NiCO, Ar-NiN_2, and Ar-CoCO than those of NiCO, NiN_2 and CoCO. These results suggest the possibility that the experimental frequencies should be attributed not to NiCO, NiN_2 and CoCO but to Ar-NiCO, Ar-NiN_2, and Ar-CoCO. In conclusion, we propose that spectroscopic data of transition metal compounds determined with the matrix isolation technique should be reinvestigated more carefully, taking into account the possibility that the target molecule makes a compound with noble gas atoms.

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A matrix isolation and theoretical study of $(SF_6)_2$ dimers spectra. The matrix structure, resonance dipole-dipole and dipole - induced dipole interactions

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This work presents the results of FTIR and theoretical studies of the $(SF_6)_2$ dimers spectra in Ar and N_2 matrices. It was shown that the triply degenerate ν_3 transitions in this dimer are split into a doublet whose characteristics are determined by the resonance dipole – dipole interaction between two SF_6 subunits. Two absorption bands are observed for $(SF_6)_2$ in Ar: one band ($\nu_{X,Y}$) is blue shifted and the other one (ν_Z) is red shifted from the ν_3 . The value of resonance splitting obtained in argon matrices $\Delta\nu = \nu_{X,Y} - \nu_Z = 18.45$ cm^{-1} is smaller than in the gas phase. The main difference between spectra recorded in Ar and N_2 matrices is the 0.9 cm^{-1} splitting of the $\nu_{X,Y}$ component in N_2 matrix. In the spectra in a molecular beam and in Ar matrix the splitting of X and Y components is not observed.

The theoretical analysis of the dimer spectra in this report includes:

1. The simple model. The main characteristics of the $(SF_6)_2$ dimer spectra in the gas phase were calculated using a simple model which takes into account the resonance dipole-dipole interaction between two point dipoles located at the centers of mass of each of SF_6 molecules and dipole-induced dipole interaction between two subunits. In this approximation $\Delta\nu_{RDD} \approx (P_3')^2 / R_{SS}^3$, P_3' is the dipole moment derivative, R_{SS} - S-S distance and $\Delta\nu_{DID} = 1.3$ cm^{-1}. But it was shown that this model can not explain the dependence of the dimers spectra on orientation of SF_6 molecules in the dimer.

2. Local mode model. The local mode model with the point dipole moments located on each of the S–F bonds of each SF_6 molecule is developed. Each dipole moment is shifted along the S-F bond by "ξ" relative the center of SF_6. This model allows to calculate the dimer spectra at various orientation of SF_6 and to take into account the solvent influence.

3. The Monte Carlo simulation. In this work the Monte Carlo simulation of the $(SF_6)_2$ dimer dissolved in matrix are done. For beginning we have calculated the structure of the matrix including rigid (SF_6) dimer and Ar (or N_2). The realistic atom-atom (Ar-Ar, Ar-S, Ar-F or N-N, N-S, N-F) pair potentials $V(R_{mn}) = B_{mn} \cdot \exp[-\Omega_{mn} R_{mn}] - A_{mn} \cdot R_{mn}^{-6}$ between all $(SF_6)_2$ atoms and matrix particles were used. We considered system with periodic boundary conditions. The modification of Metropolis algorithm was applied for 512-1440 particles in box.

The local mode model was used and dipole-induced dipole interactions between all point dipoles located on the each of the S-F bonds of $(SF_6)_2$ dimer and matrix particles were

taken into account for the dimer spectra calculation in Ar and N_2 matrices. The solution of the secular equation for $(SF_6)_2$ gives the frequencies and intensities of 12 stretching vibrations of the $(SF_6)_2$ dimer in Ar and N_2 matrices. The calculated spectra sufficiently well reproduce the main characteristics of the experimental spectra in these matrices in particular, the decrease of the resonance splitting on transition from the gas phase to Ar matrix and the splitting of ν_{XY} component in nitrogen matrix.

This study was supported by Russian Russian Foundation for Basic Research (grant N 06-03-32073)

The cryochemical synthesis of novel type of organomagnesium clusters

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More than 100 years have passed since Victor Grignard published his paper on the preparation of etherial solution of compounds in which carbon is bonded to magnesium:

$$RX+Mg=RMgX$$

However, RX with Mg interaction in solid state at low temperatures leads to the formation of cluster analogues of the Grignard reagent:

$$RX+nMg=RMg_nX$$

(R=Ph, alkyl, aryl, X=F, Cl, Br, H)

Two types of organomagnesium clusters have been obtained. They are cluster Grignard reagents and their hydride analogues. Organic clusters composition has been detected by MALDI-TOF MS. Brutto formula, RMg_4X, has been confirmed by elemental analysis. It was shown that only tetramagnesium species could be obtained.

Grignard reagents have been an obvious choice for organic chemists in a many cross-coupling reactions with organic halides. For cluster Grignard reagents various interactions can be observed in a systems organotetramagnesiumhalides – organic halides:

Cross-coupling	$PhMg_4Br+C_3H_5Br \rightarrow C_3H_5Ph$
Halogen exchange	$PhMg_4F+C_3H_5Br \rightarrow PhBr$
Catalytic halogen exchange	**$PhMg_4F$** $PhF+C_7H_{15}Cl \rightarrow C_7H_{15}F+ PhCl$
Remetallation	$PhMg_4F+C_7H_{15}Cl \rightarrow C_7H_{15}Mg_4Cl+PhCl$
Catalytic isomerization of alkylchlorides	**$PhMg_4F$** $n\text{-}C_7H_{15}Cl \rightarrow i\text{-}C_7H_{15}Cl$

Unusual catalytic properties of organopolymagnesium hydrides have been found in various reactions that involve C-H and C-C bonds, for example, isomerization of alkenes, autohydrogenolysis of unsaturated hydrocarbons.

The regularities of stabilization, reactivity and catalytic activity of organomagnesium clusters are discussed.

Mechanism of UV-photodissociation of van der Waals clusters $(CH_3I)_2$ and $(HI)_2$

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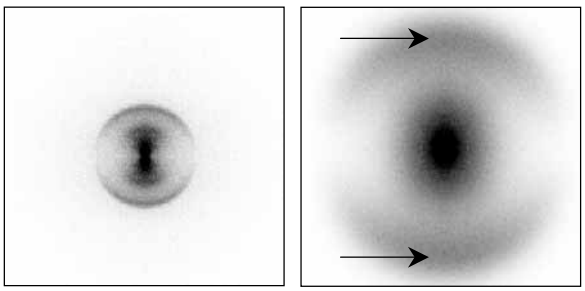
UV-photodissociation of van der Waals dimers $(RI)_2$ of iodine containing molecules is the most documented example of the so-called "concerted photochemistry" when new photochemical channels become open as to compare with the photodissocaition of individual molecules RI.

It is well known that UV-photoexcitation of individual molecules RI leads to the photodissociation with the formation of R and I as a photoproducts. The analogous excitation of clustered RI gives rise to the additional channels of the photodissociation that result in the formation of neutral and ionized molecular iodine. The observation of the formation of I_2 and I_2^+ following the UV-photoexcitation of clustered RI has been reported in the literature by many authors. But despite of the big interest to this "concerted photochemistry" the mechanism of the formation of those products has not been totally understood.



The velocity maps of I^+ arising in the photoexcitation of unclustered (a) and clustered (b) CH_3I at the wavelength of 248 nm demonstrate the dramatic differences. In the case of clusters the new channel of the formation of I^+ (indicated by the arrows) with the kinetic energy about 1 eV appear due to the "concerted" photochemistry.

The present study has been aimed at the detailed investigation of photodissociation of van der Waals dimers $(CH_3I)_2$ and $(HI)_2$ at the wavelengths around 250 nm. In our study the attention has been paid to the detailed characterization of the arising photochemical products and to the revealing of the mechanism of the formation of those products.

Clusters $(CH_3I)_2$ and $(HI)_2$ were prepared with using of the technique of supersonic jet cooling. Photoexcitation of clusters was provided by the radiation of nanosecond pulsed laser (excimer KrF or second harmonic of tunable dye laser).

The nascent photoproducts were registered and analyzed with using of a time-of-flight mass spectrometer and a velocity map imaging technique. This technique provides the detailed measurement of the speed and angular distributions of the photoproducts.

In our experiments we observed and characterized two ionic photoproducts I^+ and I_2^+. The speed distribution of ions I^+ revealed the new channel of the formation of I^+ as to compare with the photodissociation of individual molecules (see the figure).

Based on the obtained results we suggested the mechanism of the photodissociation of dimers $(CH_3I)_2$ and $(HI)_2$ that explains the formation of the observed photoproducts I^+ and I_2^+.

Acknowledgement. The financial support of this work by the Netherlands Organization for Scientific Research (NWO), Russian Foundation for Basic Research (Grant N 02-03-32001) and Siberian Branch of RAS (Interdisciplinary grant № 62) is gratefully acknowledged.

Chapter 3

Posters

Cryochemical preparation and investigation of silver ultrafine particles in acetonitrile and pyridine

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Silver ultrafine particles (UFP's) in acetonitrile and pyridine have been prepared by cryochemical method in this work.

Silver vapors have been deposited at low temperatures under vacuum (10^{-4} Torr) with excess of organic solvents. Condensation velocity of silver vapors was 10^{12} – 10^{13} atoms/($s \cdot cm^2$) and of organic solvent vapors about 10^{16} molecules/($s \cdot cm^2$). After melting of deposits colloidal solutions have been obtained. All manipulations with prepared silver solutions have been done in air atmosphere at room temperature. Properties of silver UFP's have been investigated by different techniques among them X-Ray Powder Diffraction (XRD), Photon Correlation Spectroscopy (PCS), UV-visible spectroscopy, Transmission Electron Microscopy (TEM).

Silver colloidal solutions in **acetonitrile** with silver content 0,2 mg/ml were brown in color and were stable for some months. Absorption bands at 220-270 nm and broad absorption band with maximum at 420 nm were observed in spectrum of colloidal solution with silver content 0,2 mg/ml. Intensive broad absorption band with maximum 420 nm corresponds to plasmon absorption of silver. XRD showed presence of Ag and Ag_2O. Determined by X-Ray Diffraction line broadening average size of crystallites was 21 nm. TEM investigation showed that large silver clusters in acetonitrile have fractal structure.

Silver colloidal solutions in **pyridine** were dark-brown in color. Two broad absorption bands with maximums at 365 nm and 510 nm were observed in spectrum of solution with silver content 0,8 mg/ml. Broad absorption band with maximum at 340 nm and broad absorption band without maximum in region 400 – 800 nm were observed in spectrum of colloidal solution with silver content 0,4 mg/ml. Broad absorption bands correspond to wide particle size distribution. Absorption in region at wave lengths less than 380 nm corresponds to absorption of small silver clusters with number of atoms less than 12. The maximum in short wave region shifted to 300 nm one day later. One day later after preparation optical density of silver – pyridine solutions at λ = 364 nm decreased 2,5 – 3 - fold and then remained constant.

Size distribution of silver aggregates in pyridine solution with metal content 0,8 mg/ml was determined by PCS. Average size of silver aggregates was 361 nm. Investigation of silver particles obtained from this sample by XRD showed presence silver phase only. Line broadening was very little. This result due to formation of large crystallites (more than 50 nm). Investigation of silver particles obtained from other sample (metal content 0,4 mg/ml) by XRD showed presence of Ag and Ag_2O. Determined by X-Ray Diffraction line broadening average size of crystallites was 35 nm. Thus decreasing of silver content leads to decreasing of crystallite average size and to increasing of reactivity of silver UFP's with air oxygen.

Thus cryochemical method leads to relatively stable silver colloidal solutions in acetonitrile and pyridine.

Properties of Low-Temperature Spectral Relaxation in Proteins and Viscous Media

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The role of molecular solvation dynamics in electron transfer (ET) kinetics has been intensively investigated for recent years. One of the most useful methods for investigation of molecular dynamics in polar media is the phosphorescence probe method. On the base of relaxation kinetics of probe phosphorescence spectra shifts it is possible to obtain important information about orientational mobility in medium, solvation processes dynamics in polar solutions. Eosin was used as the phosphorescence probe. Kinetics of relaxation shifts of eosin phosphorescence spectra has been measured in 60 % water-glycerol solution and in modified eosin-hemoglobin complex in 100-250 K temperature range.

The method of spectral reconstruction was used to obtain instantaneous phosphorescence spectra. The shape of instantaneous phosphorescence spectra was fitted with polynomial. Instantaneous phosphorescence spectra were used to calculate the normalized correlation function of dynamic Stokes shift of the phosphorescence spectrum:

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

An interesting feature of the correlation function was the fact that it did not attain the value of C(∞) = 0 in the long time limit at several temperatures somewhat above the glass transition temperatures. Therefore, experimental C(t)'s were fitted to the following expression:

$$C(t) = \int_0^{\tau_0} g(\tau)\exp(-t/\tau)d\tau + \Delta C,$$

where ΔC is a temperature-dependent constant, accounting for the difference between the value of experimental C(t→∞) and C(∞) = 0; g(τ) - the Cole-Davidson distribution function, τ - the relaxation time.

For all measured systems the kinetics occurred nonexponential that proves existence of relaxation time distribution in water-glycerol solutions and in proteins. The special computer program has been done for describing nonexponential characteristic functions in the framework of Cole-Davidson distribution. The parameters of this distribution were determined.

The measurement of the dynamic Stokes shift of phosphorescence spectra is an efficient method for studying the relaxation dynamics on viscous media and proteins at low temperatures.

The values of τ and τ_0 are in good accordance with the data obtained by different techniques and may be used in describing of ET reaction in the systems under investigation (glycerol, isopropanol, haemoglobin).

The activation energies of the relaxation dynamics in the investigated systems were obtained.

The investigations were supported by RFBR grants and by grant CRDF # RUC2-2658-MO-05.

Matrix IR and Computational Study of HCN…C_2H_4…CO complexes

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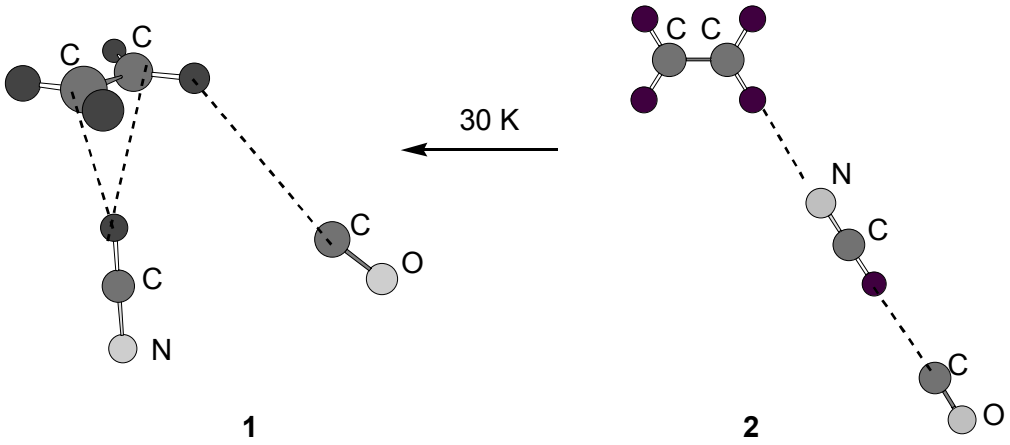
Hydrogen-bonded 3-molecular complexes of HC≡N with $H_2C{=}CH_2$ and CO, were generated in Ar matrices at 12 K by full light photolysis of cyclopropylcarbonyl azide and were identified using FTIR spectroscopy. The molecular structure and vibrational frequencies of the complexes were calculated at the B3LYP levels of theory by employing basis sets ranging from 6-31G(d) to 6-311++G(2d,2p). Computations and experiments showed that two types of complexes 1 and 2 are formed. The more stable complex 1 has a T-type structure. Analysis of IR spectra suggest the less stable linear complex 2 rearranges into T-type complex upon matrix annealing.



We thank the following for financial support: the President of Russian Federation (Presidential Program for support of leading Research schools, Grant NSh-6075.2006.3), Russian Academy of Sciences (Programs P-09 and OKh-01).

Low-temperature formation of nanostructured films by co-condensation of Pb with CO_2

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Recently the gas sensitivity of nanostructured Lead thin films has been detected for water and ammonia vapors. These films were prepared by vacuum depostition on insulating substrates at 80 K and futher annealing to room temerature. It was found that the film structure and properties were affected by the deposition and annealing conditions. Thus, by changing the flux it one is able to produce sensitive and insensitive films with the same amount of lead and very different microstructure [1].

The present work was aimed at decreasing the Lead nanoparticle size by using a co-deposition of its vapors with carbon dioxide at 80 K. The solid co-condensates were studied by low-temperature IR-spectroscopy. After annealing the samples were investigated by Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). The sensitivity to water and ammonia vapors was studied by electrical conductance measurements using Keithley 6517A electrometer.

Nanostructured thin films obtained after the sublimation of carbon dioxide were found to possess approximately the same sensitivity to water vapors, as the samples, prepared without CO_2. Thus, the resistance of the samples decreases by 3-4 orders of magnitude when relative humidity is changed from 5 to 95 %. Though, the mean particle size was smaller – from 13 to 33 nm in different samples. As a result of decreasing the size of Lead particles, the sensitivity range for humidity broadened. This fact is consistent with the capillary condensation model, where condensation starts earlier for smaller pores.

The results thus obtained indicate that the low-temeperature co-deposition of metal vapors with inert gases followed by controlled gas sublimation can be used for preparation of smaller nanoparticles. The parameters of cryocondensation and carbon dioxide sublimation allow influencing the particle size.

The work was partially supported by RFBR grant 05-03-32293.

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Dimethylvinyl(ethynyl)carbene: matrix IR and quantum-chemical study

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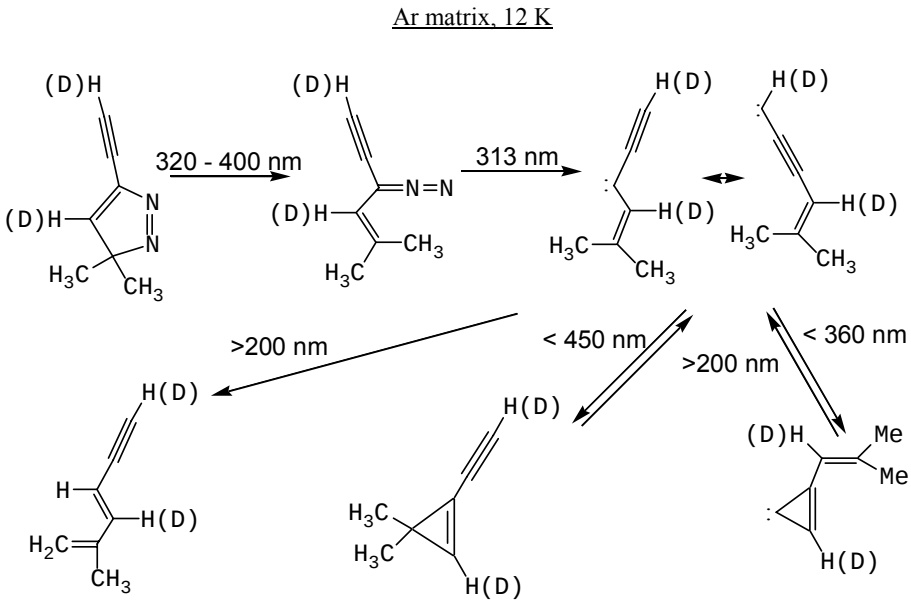
The first representative of carbenes bearing both vinyl and ethynyl substituents at the carbene center has been observed by IR spectroscopy in low-temperature Ar matrix.



It has been found that the further photochemical transformations of the triplet dimethylvinyl(ethynyl)carbene are those more characteristic of vinylcarbenes rather than ethynylcarbenes, viz photoisomerization of the carbene into the corresponding vinylcyclopropenylidene is the minor process only, while the major process is its rearrangement to ethynylcyclopropene. Both products are unstable to UV irradiation and slowly convert to dienyne. Assignment of the IR bands of all the observed species has been carried out with aid of DFT PBE/TZ2P calculations.

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New experimental approach for creation of radicals in gas jet injected into superfluid helium

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Impurity-helium condensates – new nanomaterials are produced by injection of helium gas jet containing impurities (heavier noble gases, molecular nitrogen, deuterium, etc.) into superfluid helium (HeII). A dissociation of molecular admixtures allows to stabilize high concentrations of radicals and to study chemical reactions at temperature 1.5-15 K. A radiofrequency (RF) discharge (40 MHz, 20-100 W) is effective means to dissociate and excite impurity particles, but such disadvantages as a device fragility and high power release exclude any possibility of RF discharge application in some cases. We have applied high voltage (0.6 – 6 kV) DC-discharge to excite and dissociate impurity particles in gas jet striking the surface of superfluid helium. Emission from excited particles in the crater formed at the surface by the gas jet was detected.

The kinetics of metastable helium species is well studied in both gaseous and liquid helium. Addition of impurity in helium gas quenches intense emission from He* and He^*_2 in gas discharge due to Penning ionization of impurity atoms and molecules. Spectral changes caused by addition of 1 % of neon to gas helium jet are shown in Fig.1. Addition of 1 % of molecular nitrogen completely quenched emission of excited helium particles (Fig.2). Bands both of molecular nitrogen ion, $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$, and of nitrogen molecule, $N_2(B^3\Pi_g \rightarrow A^3\Sigma^+_u)$ and $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$, dominated in the observed spectra.

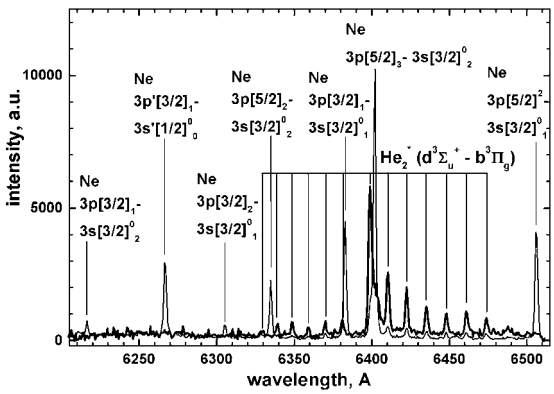

Fig. 1. Spectral changes caused by addition of 1 % of neon to gas helium jet.

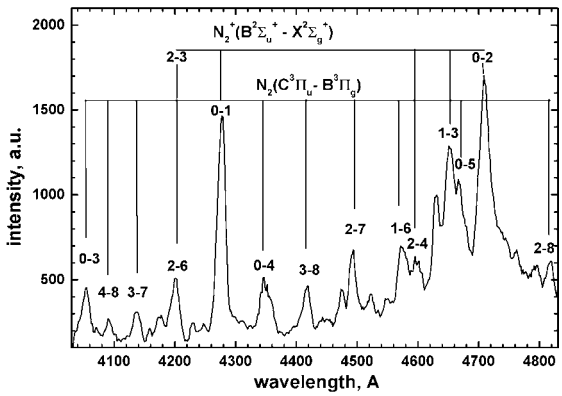

Fig. 2. Spectra of excited nitrogen species above the surface of HeII.

The closeness of molecular nitrogen ions to the surface of HeII is very promising for spectroscopic and mobility studies of these ions in bulk HeII. We suggest also to use other impurities in our studies.

A presence of high concentrations of nitrogen atoms stabilized in nitrogen-helium samples was revealed during destruction of the samples due to intensive emission on $N(^2D \rightarrow {}^4S)$ transition.

Accurate calculations of spectra of biological chromophores by ab initio methods of quantum chemistry

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Photoactive proteins containing light-absorbing organic chromophores play a crucial role in living organisms. In particular, they include the photosensors, whose activation is based on light-induced izomerization as in Rhodopsin, located in the eye retina, or in Photoactive Yellow Protein (PIP), responsible for initiating signaling cascades that leads purple halophilic bacteria to avoid blue light. Further important members are light converters which emit light as a consequence of the primary photoexcitation as in Green Fluorescent Protein (GFP) like proteins, widely used in biology and medicine as biomarkers in vivo.

Modern spectroscopy tools are intensively used to gain the knowledge of events occurring upon photoexcitation of organic chromophores in various media, and low temperature experimental conditions are often helpful in assigning spectral properties of fluorescent proteins. Although the organic chromophores function in proteins, knowledge of their spectral properties in the gas-phase is highly valuable since it provides important reference data for comparison to condense phase conditions. Recent measurements of spectral properties for the series of ionized chromophores in vacuo by the Aarhus group are of exceptional value in this respect. In particular, the positions of the bands λ_{max} for the retinal chromophore in the protonated Shiff-base form from Rhodopsin, the chromophores from PYP and from GFP have been reported. The authors challenge theoreticians by stating that "the measured S0-S1 transition wavelengths may be used as a new benchmark values for theory".

Modern quantum calculations of the excitation energies in large molecules employ either multiconfigurational based approximations to the wavefunctions or the less expensive response methods like time dependent density functional theory (TDDFT). In this communication we report successful developments toward quantitative evaluation of absorption S0-S1 peaks λ_{max} of biological chromophores in vacuo by using state-of-art multiconfigurational methods of quantum theory. The errors of the new approach may be estimated as less than 0.07 eV in energy or 10 nm in band positions in this range. In brief, the theory is based on the multiconfigurational quasidegenerate perturbation theory of the second order combined with the theory of effective Hamiltonians of extended dimensions. The theory is implemented to the PC GAMESS (Alex Granovsky) program system of quantum chemistry.

This work is supported in part by the grant from the Russian Foundation for Basic Research (05-03-39010).

Resonance cooperative effects in spectra of the low-temperature solutions and liquids

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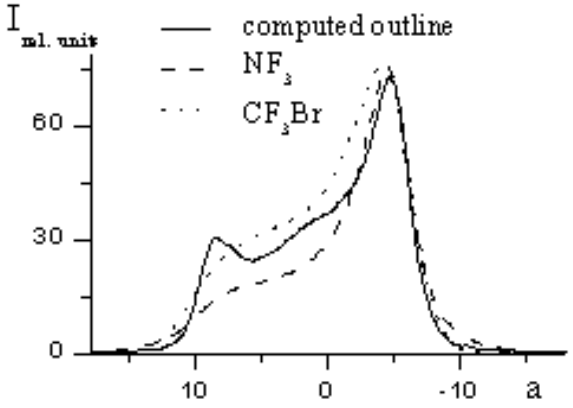
In the low-temperature liquids the resonant dipole-dipole (RDD) interaction of molecules with large first derivative of the dipole momentum (≥0.3D), leads to the pronounced dependence of definite bands properties on the environment [1]. IR absorption spectra for the number of the low-temperature liquids (SF_6, CF_4, SiF_4, NF_3, CF_3H, CF_3Cl, CF_3Br, OCS, CO_2, N_2O) were obtained in [2]. Besides with the bands with the symmetric, Lorenz-like profiles, with characteristics being goverened by the rotational relaxation, the bands with the rather complex, broad profiles (50-100cm^{-1}) were also observed. This fact definitly may be explained by the RDD intermolecular interaction. A spectral function of these profiles is described by the solution of the secular equation within the basis of the vibrational states of N equivalent molecules.

In order to calculate properly the profiles, we have developed the program being based on the accounting of the RDD interactions of N molecules, where N varies from 2 (dimers [3]) to 68. The first (N=12) and the second coordinating spheres have been considered. The orientation of molecules is random. Variations of the intermolecular distances R have normal distribution: $y \approx \frac{1}{2\pi}\exp(-\frac{x^2}{2\sigma^2})$. Up to 1000 random configurations are realized. Computed profiles are in reasonable agreement with the experimental ones:



Due to high sensitivity of profiles' characteristics (the second and the third spectral moments) to both R and N values the short range order parameters of a liquid may be determined by the vibrational spectroscopy.

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Electron Emission from Rare Gas Solids Observed by EPR Experiment

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Unstable signals are observed when discharge products of a gaseous Ne are condensed on a substrate located at the center of an EPR microwave cavity. The spectrum disappears at the moment the discharge is turned off. The main feature of the spectrum is a narrow (~ 0.1 – 0.2 G) line with g = 2,000. We have found that the signal amplitude changed insignificantly when the substrate temperature increased from 4.2 to 7 K. Subsequent rise in this temperature resulted in considerable drop of the amplitude. An essential finding lies in the fact that the unstable line while being of a very small amplitude stop to decrease at a temperature above approximately 11.5 K. Obviously, no Ne gas condenses on the substrate at such a high temperatures. The fact that the signal amplitude depends on the substrate temperature suggests that the unstable spectrum is due to processes occurring in the solid gas layer. Hence, the signals observed at temperatures above 11.5 K are due to residual gas solid layers. In order to verify this assumption, a gaseous Ar was supplied onto the substrate through an inlet tube avoiding the gas discharge running in Ne. We observed an abrupt large increase in the signal amplitude to the value even greater than the initial one with solid Ne on the substrate. The line was again of very small amplitude when the substrate temperature grew above the Ar sublimation temperature. We substituted then the Ar gas flow by the Kr flow and proceeded with the substrate temperature increase. The changes in the line amplitude were the same as with the Ar experiment. The g-factor of the line shows no depend on a kind of the gas passed through the inlet tube. The same result was observed at the substrate temperature varied below 4.2 K [1]. We observed no change in the signal amplitude when a gaseous CO was supplied instead of Ar or Kr. The whole set of experimental data may be noncontradictory explained with an assumption that the observed signal with g = 2,000 is due to the cyclotron resonance of free electrons emitted from a solid gas layer being subjected to the gas discharge irradiation. An analysis of the linewidth and the spectrum structure [1] allows rough estimate of both the free electron density, ~ 10^9 cm^{-3}, and the lower limit of the electron kinetic energy, ~ 200 K to be made. The process of photon stimulated electron emission from the rare gas solids is discussed. Also discussed is an effect of the O_2 impurity concentration [1] on the electron emission from the rare gas solids.

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Low Temperature FTIR and DFT Studies of the Intereaction between Acetylhalides and Aluminium Halides

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The interaction between dimeric aluminum chloride and bromide with acetylhalides was studied by low temperature FTIR spectroscopy. The components were successively deposited at 77 K on a KRS-5 support in a specially designed low temperature cell, the film was annealed to allow the component diffusion, then the cell was slowly warmed inside the spectrometer, and the reaction was monitored by IR spectra. Low temperature FTIR spectra in the low frequency range were first recorded for the systems studied.

The formation of several novel unstable donor-acceptor complexes between the components was detected. Quantum chemical DFT/PBE calculations of optimal geometry, energy, and vibrational frequencies were performed in 3z basis set using “Priroda” program package [1].

The structure of novel complexes was proposed on the base of the analysis of experimental and calculated spectra. The analysis of the spectra in the ν(CO) and ν(Al-Hal) ranges shows that only weak donor-acceptor complexes formed at low temperature contain dimeric aluminum halide molecule with two halide bridges. On increasing the temperature, at first one Al-Hal-Al bridge breaks to form a complex with a distorted dimeric aluminum halide molecule with one halide bridge. On further temperature increase both halide bridges break to yield a 1:2 donor-acceptor complex containing two $AlHal_3$ fragments bound to the oxygen and halide atoms of acetyl halide and known 1:1 donor-acceptor complex containing $AlHal_3$ molecule bound to the oxygen atom. Further temperature increase leads to the formation of ionic complex $[CH_3CO]^+ [AlX_4]^-$.

Novel unstable donor-acceptor complexes might be intermediates in catalytic reactions of alkane activation in the presence of acetyl halide - aluminum halide systems.

The work was supported by RFBR (grant 04-03-33117) and by the program of the Division of Chemistry and Material Sciences of RAS.

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Low-temperature postradiation living radical polymerization of vinyl monomers in presence of fullerene C_{60}

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The problems of modification and functionalization of nanomaterials to obtain their water soluble derivatives are very challenging task due to the possibility of their using in medicine and biology. In present work we have investigated low-temperature γ- induced postpolymerization of acrylic monomers such as an acrylamide (AA) and an acrylic acid (AAcid) in presence of fullerene C_{60} using optical, EPR spectroscopy and calorimetric technique. The radiation initiation has an advantage because it does not need in including into the system the substantial initiators or catalyst. This is very important for medical application of products obtained. More over the sterilization of products may take place during the irradiation.

Irradiation of mixture of acrylic monomers in ethanol with solution of fullerene in toluene has been carried out at 77K. It has been shown that polymer chain growth took place after system transition from glassy state into viscous overcoold liquid during the heating of irradiated at 77K samples. Propagating polymer chains being able to grow quickly turned out to be stable in the conditions of overcoold liquid, i.e. macroradicals R_p do not terminate. So, the process performs according to mechanism of living radical polymerization. During polymerization of acrylic monomers in presence of C_{60} the concentration of propagating macroradicals is lower ($Rp \rightarrow 0.15R_0$) than that for polymerization of AA and AAcid without fullerene in the same conditions (($Rp \rightarrow 0.4R_0$). The yields of pure polymers of AA and AAcid (PAA, PAAcid) obtained in identical conditions turned out to be ~98% and 57%, while the yields of fullerene containing polymers FPAA and FPAAcid equal to 72% and 21%, respectively. The reason for efficiency decreasing may be that after fullerene molecules addition to the macroradical Rp latter becomes inactive because of delocalization of unpaired electron on conjugated system. 93 % of fullerene molecules interacted forming both fullerene containing polymer and, possibly homopolymer contained in a residue (3%). C_{60} abundance in water soluble part of product turned out to be ~0.5 %.

The work was supported by RFBR (grant № 06-03-32898).

Studies of New Resonance Features in the IR Collision-Induced Spectra of Molecular Hydrogens in Liquid Neon

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Results of quantitative studies of collision-induced IR fundamental absorption of all stable hydrogen isotopomers (H_2, D_2 and HD) dissolved in liquid Ne (T≈25 K) are reported. The accent is made on the new, unusually sharp $Q_1^q(J)$ (*J=0,1*) lines developing on the diffuse background produced by the damped intracell oscillations of the solute. In all spectra studied, an observed parabolic intensity growth with the solute concentration *x* is accompanied by considerable narrowing of the Q_1^q doublet components. Multi-parameter fittings of the overall spectral distributions are performed aiming at the accurate separation of the Q_1^q profiles. The use of the catalyst (hydrated iron(III)oxide) allows to get rid of the *ortho* species signatures and considerably simplifies the spectrum structure. The *para* - H_2 $Q_1^q(0)$ shape analysis shows how the guest-host contribution dominating at small *x* becomes gradually masked by the sharper guest-guest feature that leads to overall concentration narrowing. Arguments are given in favor of the diffusional nature of the guest-guest component which is further supported by the D_2 and HD spectral data. First observation of the $U_1(J)$ transitions induced by the H_2-Ne interactions is also reported.

The authors thank the Special Research Fund of the University of Antwerp, the FWO-Vlaanderen and the Russian Foundation for Basic Research for financial support.

An FTIR and ab initio study of $CClF_2H$ and its weak hydrogen bonded complex with CD_3F

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The mid- and near-infrared spectra of solutions in liquid krypton containing $CClF_2H$ and mixtures of $CClF_2H$ and CD_3F are investigated. Apart from the bands assigned to the monomer species, in the spectra of the mixed solutions new bands due to a C-H···F hydrogen bonded species are observed. The C-H bond involved in the C-H···F hydrogen bond is characterized by a blue shift of approximately 25 cm^{-1}, and a strong decrease of its infrared intensity, the ratio between monomer and complex being xx.x(x). The appearance of a blue shift and a significant decrease of the infrared intensity proves that the complex between $CClF_2H$ and CD_3F must be classified as a improper hydrogen bond.

The relative stability of the complex was determined using temperature studies, in which the temperature dependence of the monomer complex intensities was evaluated, at temperatures varying from 118 to 163K. The resulting complexation enthalpy equals -7.8(5) kJ mol^{-1}.

The experimental studies are supported by ab initio calculations in which the properties of the monomers and of the complexes are studied, using a variety of levels and methodologies. The results show that, apart from the main CH···F interaction, secondary interactions are present in which the fluorine of the chlorine atoms located in the haloform interact with the hydrogen atoms of the proton acceptor.

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Glass-like behavior of thermal conductivity of $CH_4 – CD_4$ solid solutions

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Some mixed crystals demonstrate their low-temperature thermal properties being like that for amorphous solids. This phenomenon is usually ascribed to a disorder of another kind – a non-translational disorder. Here we report results of measurements of thermal conductivity of $CH_4 – CD_4$ solid solutions which display glass-like behavior for some concentrations of deuterated methane. In this case, however, the disorder existing at these concentrations of CD_4 cannot account for the characteristic plateau. Instead, we explain it as a result of enhancement of phonon-rotation interaction being a consequence of lowering of the symmetry of molecular field.

Autowave Regime of Polymerization of Epichlorohydrin Initiated by Local Brittle Fracture of Solid Samples at 4.2–77 K

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If crystalline and glassy epichlorohydrin (ECH) is exposed to gamma-radiation at 4,2-77 K, active polymerization centres accumulate. If the pre-irradiated samples do not have local indignations (brittle fractures), the monomer polymerizes when heated further. Polymerization mainly occurs in the region of devitrification – T_g = 130 K (for glassy ECH) or melting of monomer T_m = 210 K (for crystalline ECH) [1]. Local fracture of samples irradiated by the dose higher than critical value gives the opportunity to implement the autowave mode of transformation in the glassy ECH at 4.2-77 K. The polymerization wave arises at the threshold γ-irradiation dose of 140 kGy. The reaction of polymerization "switches on" when creating a local indignation; the temperature in the wave front rapidly ($\tau \sim 0.1$ s) reaches its maximum value (150-160 K for the pre-irradiation dose of 140-400 kGy). The width of the running wave front is ~ 1-2 mm; the critical value of temperature gradient is $dT/dx \approx 20$ K/mm. The speed of spreading of wave front of polymerization EPH increases from 3 up to 20 mm/s with the increase of preirradiation dose at 77 K (140-400 kGy). The yield of polymer is 9-13%. The resulted characteristics of polymerization wave evidences the implementation of mechanism proposed in [2, 3]. According to it, the mechanical energy of resilient deformation saved in solid matrix expenses at the moment of brittle fracture. The energy is used to form chemically active intermediate stations and increase the molecular mobility of reagents. The self-supported regime of transformation appears as a result of positive reverse connection between the chemical transformation in a solid and its brittle fracture lead by the temperature and density gradients appeared during the reaction.

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EPR and Optical Spectroscopic Studies of Diketone Radical Cations in Low-Temperature Matrices

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Bifunctional radical cations provide an interesting model for investigation of long-range interactions and electron transfer in radiation chemistry and photochemistry of complex organic systems. Due to their high reactivity, these species can be studied only in rigid and chamicaly inert media at low temperatures. In this work we present the results of the spectroscopic studies of radical cations of some diketones, where two ketone groups are separated with methylene "bridge" of different length:

$Y–C(O)–(X)_n–C(O)–CH_3$, where n = 0, 1, 2 X = $–CH_2–$ Y = $CH_3–$
n = 1, X = $–CH(CH_3)–$ Y = $CH_3–$
n = 0 Y = $C_2H_5–$

The radical cations were generated by X-ray irradiation of the frozen Freon solution of the investigated substances at 77 K and characterized by EPR and electron absrption spectroscopy. The experimental hyperfine coupling constants were compared with the results of the DFT calculations.

Special measures were taken to avoid uncontrolled photochemical reactions of the solute species. The photosensitivity of the irradiated samples to UV/visible light was monitored by parallel EPR and optical absorption measurements. After photolysis some of the most photostable samples were heated to the temperatures up to 140 K and then the EPR spectra were measured again.

In most cases, the obtained spectra reveal considerable g-factor anisotropy. For this reason, one can make a conclusion that major spin density is located on carbonyl groups (assuming delocalization between the two functional groups, which is supported by the quantum chemical calculations). Also, it was found that observable hyperfine splittings in EPR spectra (if any) were due to relatively large spin density on specific "bridge" hydrogen atoms. In the cases of diacetyl and 2,3-pentandione, all the proton hyperfine coupling constants are small (comparable with the experimental linewidth).

Most of the diketone radical cations studied in this work were found to be rather stable under visible light irradiation. Also, heating up to 140 K did not show appreciable effect on the EPR spectra. In contrast to this observation, the radical cations of 2,5-hexanedione (n = 2) and 2,3-pentanedione (n = 0, Y = $C_2H_5–$), showed considerable changes in the EPR spectra after 7 minutes of photolysis with a 400±30 nm light. These changes were explained by intramolecular hydrogen atom transfer to the carbonyl oxygen atom. This work was supported by the Russian Foundation for Basic Research (project no. 06-03-33104).

Vibrational spectra and structure of NO-H_2O, NO-HDO and NO-D_2O complexes. An IR matrix isolation and DFT study

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The infrared spectra of H_2O + NO isolated in solid neon at low temperature have been investigated. The H_2O + NO system is remarkable due to its propensity to form NO-H_2O, $(NO)_2$-H_2O, NO-$(H_2O)_2$ and NO-$(H_2O)_n$, and IR spectroscopy reveals a variety of phenomena far from being fully understood. We will focus here on the NO-H_2O and NO-$(H_2O)_2$ species.

Low concentration studies (0.01 % - 0.2%) and subsequent annealing leads to the formation of one NO-H_2O complex in which NO is weakly bonded to H_2O. All Vibrational modes of this complex have been detected. In addition, spectra of D_2O + NO and HDO + NO have also been recorded. A detailed vibrational analysis of deuterated species shows that two species NO-$D_2O(\alpha)$ and NO-$D_2O(\beta)$ have been observed. One species NO-$D_2O(\alpha)$ is similar to the observed NO-H_2O and another species NO-$D_2O(\beta)$, which structure has been predicted by DFT calculations, where the water deuterium and the NO nitrogen are weakly bonded. The NO-$H_2O(\alpha)$ and NO-$D_2O(\alpha)$ potential surface was explored systematically at the B3LYP level but no stable species reproducing the experimental data could be found. This shows that the structure of the observed NO-$H_2O(\alpha)$ and NO-$D_2O(\alpha)$ species results from columbic attractions between the water and NO and is stabilized only in neon matrix.

The Investigation of Low-Temperature Radiation Polymerization and Nature of Active Sites in the System Methylmethacrylate-Silica Dioxide

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The radiation- initiated heterogeneous polymerization onto the surface of porous silicas attaches attention as a method of creation of new polymer compositions which possesses a variety of unique properties. The method of differential scanning calorimetry, ESR- and IR-spectroscopy were used to investigate the process of a low-temperature post-irradiation polymerization of methylmethacrylate (MMA) sorbed into macroporous glass (SiO_2). It was observed the high efficiency of polymerization of MMA in sorbed station at low temperature (in the region 160-250 K). At the preirradiation dose 10 kGy the conversion of monomer is 100 %, and the yield of homopolymer not exceed 18 % [1] (whereas in high temperature process this yield usually reaches not less than 50 % [2]) . The paramagnetic sites formed at the low temperature (77 K) radiolysis of SiO_2 and MMA have an ionic and radical nature. Polymerization of sorbed MMA (at the radical mechanism of growing of polymer chains) initiates mainly by the ions, the quantity of which (the data of photobleaching) is more than 90 %. The contribution of radicals (->$Si^{\cdot}$; >$Si^{\cdot}$ - H; H-$Si^{\cdot}$=O) in the common concentration of active sites not exceed 3 %. Supposing the ion mechanism of initiating it is need assume that the initial stage of a graft polymerization involves the interaction between an ion at the silica support and a monomer molecule with the formation of a radical. At the ion mechanism of initiating the radiation-chemical yields of original radicals performing in the terminal-radicals of growing polymer chains in radiolized system SiO_2 + MMA at 77 K, reaches an anomalous high values : G = 53-55 1/100 eV.

The resulted polymer not soluble in benzene, toluene and inorganic acids: partly (up to 15-18 %) soluble in acetone. The IR spectra of polymer film of soluble in acetone part was detected. The absorbtion at 801 cm^{-1} belonging to valency vibration of Si-C bond allow to suggest existing of chemical bond between the grafted polymer and SiO_2 support.

The work was supported by the Russian Foundation for Basic Research (Project RFBR 06-03-32898).

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Neutralization of solvated protons in noble-gas matrices: Evidence of mobile electrons

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The $(NgHNg)^+$ cations (Ng = Ar and Kr) produced via UV-photolysis of HX/Ng (X=F,Cl,Br and Ng=Ar,Kr) solid mixtures are studied with respect to their decay mechanism. The present experiments provide a large variety of the parameters of the decay phenomenon, which is not always consistent with the results reported earlier for differently prepared matrixes. This leads us to reconsidering the previously suggested models for the decay of the cations in noble-gas matrixes. As a result, we propose that this phenomenon could be explained by neutralization of the solvated proton by electrons. The mechanism of this neutralization reaction is probably tunneling of an electron from an electronegative fragment to a $(NgHNg)^+$ cation. The proposed electron tunneling mechanism should be considered as an alternative to the literature models based on tunneling-assisted or radiation-induced mobility of protons in noble-gas lattices. We investigated also both experimentally and computationally the N_2 complexes of $(NgHNg)^+$. The observed similar decay of $(NgHNg)^+$ and its N_2 complex indicates that the solvated proton is unable to tunnel and is therefore immobile in noble-gas matrices. This further supports the electron neutralization mechanism. Another evidence for mobile electrons is provided by the annealing-induced formation of $(YHY)^-$ anions.

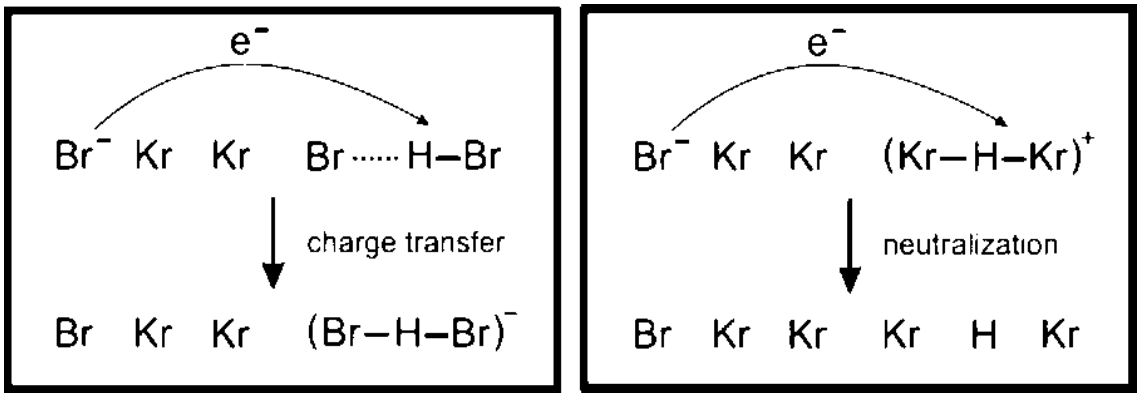

Fig. 1 A schematic view of a formation of $(YHY)^-$ (Y=Cl,Br) anions and a decay of $(NgHNg)^+$ cations by electron tunneling mechanism in noble-gas matrices.

This work is presented in following articles:

L. Khriachtchev, A. Lignell and M. Räsänen, *J.Chem.Phys.* 123, 064507 (2005)

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Preparation of macroporous and super macroporous polymeric gels using principles of cryotropic gelation and implementation of resulting materials – cryogels – in modern biotechnology

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Cryotropic gelation is a specific type of gel-formation occurring as a result of cryogenic treatment (non-deep freezing – frozen storage – thawing) of the initial systems potentially capable of gelling. The final polymeric materials thus formed have been termed as ***cryogels*** [1]. The latter ones could be of two major types: *macroporous* (the large pores with size of about 0.1-10 μm) and *supermacroporous* (gigaporous) sponge-like cryogels (they have gross pores with size from tens to hundreds μm). The large-size pores in cryogels are interconnected, since during cryotropic gelation the polycrystals of frozen solvent play a role of pore-forming agents (porogens), and each crystal grows until a tight contact with a faucet of another crystal. Just such character of morphology of various cryogels makes them attractive materials for application in many fields, in particular, in biotechnology. The porosity features of cryogels allow creating the gel matrices suitable for elaboration of highly efficient immobilised biocatalysts (based on both immobilised enzymes and whole cells), chromatographic resins that could be used in dealing with biological nano and micro particles (plasmids, viruses, organelles, cells), and polymeric supports (scaffolds) for cultivation of animal cells. The merits of cryogels in these areas are exemplified in the given report. All such materials are of great significance for modern biotechnology [2]. In this respect, for the judicious biotechnological implementation of diverse cryogels, the comprehensive information on the regularities of cryotropic gel-formation, as well as on the factors influencing the cryogel properties, is undoubtedly required. These data were obtained from the systematic basic research of the processes giving rise to the formation of covalently cross-linked cryogels (originating from both monomeric and polymeric precursors), ionically-linked cryogels (formed from the polyelectrolytes) and non-covalent (physical) cryogels, whose 3D network is stabilized by the non-covalent bonds like hydrogen ones or hydrophobic interactions. Testing of resulting cryogel-type materials showed that principles of cryotropic gelation can be successfully employed for the preparation of various promising gel materials of biotechnological significance.

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FT-IR Matrix Isolation Spectroscopy and DFT Studies of Aliphatic Azide - Methyl Sulfides Photochemistry

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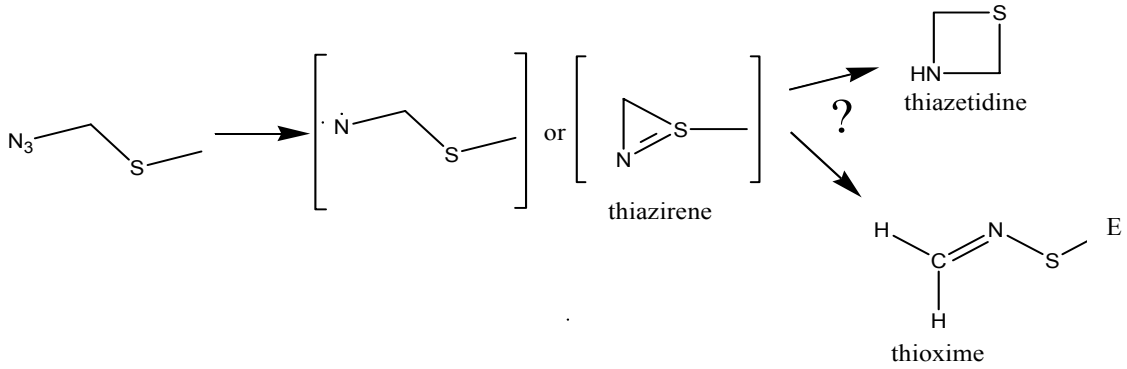
The molecular vibrations of azide methyl-methylsulfide (AMMS) were investigated by Fourier transform infrared matrix isolation spectroscopy in argon and dinitrogen matrices. In parallel, density functional theory (DFT-B3LYP) methods were used to determine the geometrical, energetic and vibrational characteristics of this compound. Its photoreactivity in Ar matrices has been studied, showing the formation of a nitrene or thiazirene as an intermediate species and a cyclic amine or thioxime as the final product. For AEMS (azide ethyl-methylsulfide), the formation of a nitrene is also observed under UV irradiation, but no amine nor imine species is detected on infrared spectra after 3 hours irradiation above 250 nm.



Abnormal bandshape transformation of ν(CH) in $CHF_3/Ar/N_2$ triple cryogenic mixtures

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The ν(CH) band of CHF_3 was studied in $CHF_3/LAr/LN_2$ triple cryogenic mixtures with variation of concentration of liquid N_2 from $x = 0$ till $x = 1$ at different temperatures (from 80 K till 110 K). The frequency of ν(CH) was founded to be changed from 3037 cm^{-1} (pure LAr) to 3051 cm^{-1} (pure LN_2 at 80K). In the mixture cryogenic solution of Ar/N_2 we observed single band at intermediate frequency with intermediate intensity. The behavior of the band was studied depending on x and T. It was shown that the band width and intensity are nonlinear functions of x.

A simple model was proposed for explanation of the observed effects. The model takes into account the relaxation processes in the liquid mixtures, it gives an opportunity to describe the observed dependence of the band shape, intensity, and frequency on the temperature and x values.

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Photochemistry of organic radical cations in solids

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The results of the investigations of the mechanisms and effectiveness of photochemical reactions of radical cations (RC) of organic compounds in different matrixes (freones, SF_6, $SnCl_4$) at 77K are presented.

Charge transfer to the molecules of the surrounding is one of the primary photochemical reaction of RC in freon matrices. If this process is energetically highly unfavorable, such as in SF_6, charge transfer to the label products of radiation-chemical transformation of the matrix can take place instead.

For the case of $Me_4Sn^{+\bullet}$ and $Me_6Sn_2^{+\bullet}$ it has been shown that the difference in the localisation of the positive charge in the ground state of the RC (Sn-C bond in $Me_4Sn^{+\bullet}$ vs. Sn-Sn bond in $Me_6Sn_2^{+\bullet}$) has no effect on the direction of the main photochemical reaction – charge transfer to the molecules if the matrix. The low values of the Sn-C bond energy in the ground state of these particles do not predetermine the reactivity of their excited states.

The measurements of the quantum yields of the proton transfer process in the photochemistry of RC have shown, that the value $\leq 10^{-3}$ are characteristic for the reaction of intermolecular proton transfer to the matrix and the products of its transformations; for the intermolecular transfer this value is $\approx 10^{-2}$, and for the intramolecular transfer - 10^{-1}.

For ethylbenzene RC, for which it is possible to stabilise individual conformers, or their mixtures, depending upon the matrix, it has been shown that photochemical transformations at 77 K are not accompanied by the changes in the conformation state of RC. However, the same type of transition in the RC of 1,4-dithiane is characterised by quite high quantum yields. This difference does not allow one to assign the changes observed to the boat – chair conformation in the RC; rather, it is likely that the process is a result of the charge transfer from RC in the boat conformation to the 1,4-dithiane molecules, which in a solids at low temperature are preferably in "chair" conformation.

For the photochemical transformations of RC of n-alkanes C_5-C_7, 1,3-dioxolane, 1,3-dioxane, 1,3,5-trioxane a possibility of matrix control of the direction and effectiveness of these processes has been demonstrated. For example, for the RC of 1,3-dioxolane the changes in the energy of the photon and the nature of the matrix allows one to register either open form of the RC, or paramagnetic complex and neutral radical (Table).

Table. Quantum yields (Φ) and the main pathways of photochemical reactions of 1,3-dioxolane radical cations (RC) at 77 K.

Reactions	Matrix	λ, nm	Φ
RC → I	SF_6	436	0,02
I → II	SF_6	436	0,2
RC → charge transfer	$CFCl_3$	436 700	0,1 0
RC → formation of paramagnetic complex	$CFCl_3$	436 700	0 0,4
RC → proton transfer	$CF_2ClCFCl_2$	436	0,08

The work is supported by Russian Foundation for Basic Research (04-03-32030).

The fluorination of organic materials at helium temperatures

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The fluorination of several synthetic (polyethylene, polypropylene, polystyrene, copolymer of ethylene and carbon monoxide, polymethylmethacrylate) and natural polymers (cellulose, lignin, and SiO_2), para-diethinylbenzene, and ethane at 20-77 K was studied by the EPR method. The low-temperature limit of reactions between molecular fluorine and hydrocarbons (solid polymers) was found to be in the range 30-45 K, that is, close to the melting point of fluorine (50 K), when the saturated vapor pressure of the halogen approached 1 torr [1]. The rate of fluorination and maximum radical concentrations depended not only on temperature but also on fluorine pressure and contact surface area, that is, the physical state of the samples. At nitrogen temperatures, the highest radical concentration were observed for high-dispersity lyophilized polystyrene, lignin, and SPL ethylene and CO at 100-150 K; these concentrations were of $(2\text{-}5)\text{x}10^{18}$ spin/g at fluorine pressures of 30-40 torr.

The reaction was controlled by the diffusion of F_2 and governed by the activationless mechanism of multicenter synchronous transition responsible for the total exothermic effect. The initiation step under cryogenic conditions was considered on the assumption of molecular fluorine participation. Minimum composition of a polymolecular complex could be determined from the structure of radical intermediates.

The work was supported by the Russian Foundation for Basic Research (Project RFBR 06-03-32898).

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Low-Temperature Radiolysis and Photolysis of 2,4,6-Triazido-3,5-Dichloropyridine

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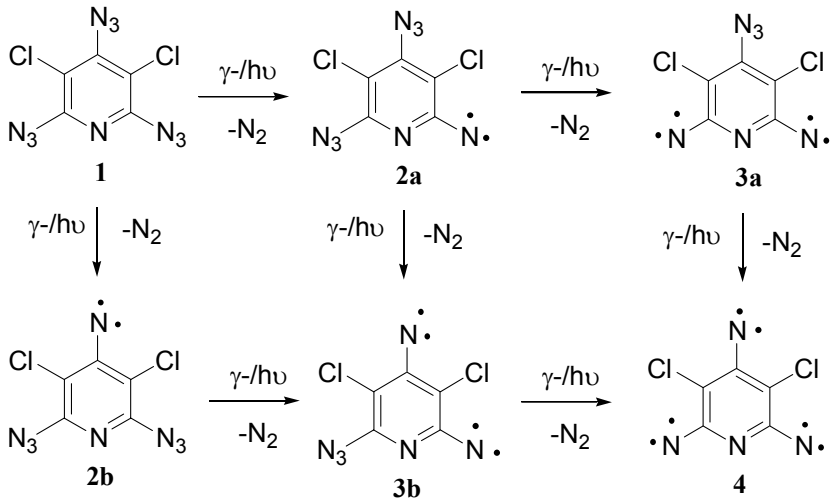
With the aim of preparing new organic magnetic materials the γ-radiolysis and UV photolysis of crystalline triazide **1** at 77 K have been studied using ESR spectroscopy. It was found that both reactions give identical paramagnetic products that were assigned to quintet dinitrenes **3a** and **3b** [1]. These quintet dinitrenes displayed the characteristic ESR signals of the Y_2-transitions at 301 and 335 mT at temperatures from 77 till 250 K. The effects of cross-saturation in ESR spectra of quintet spin-states are discussed.



The study for the first time demonstrates that low-temperature γ-radiolysis of crystalline azides can be a useful method of generation of high-spin nitrenes.

The work was supported by the Russian Foundation for Basic Research (Project RFBR 05-03-32410 and 06-03-32898).

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Cryosynthesis and physico-chemical properties of gabapentin

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Cryochemical modification is powerful method of micronization and variation of crystalline structure of organic substances, which applying to medicinal substations may lead to improvement of its bio-pharmacological properties. The essence of this method consists in vapor condensation on cold copper surfaces (80-298 K) with consequent heating to required temperature. Chemical and physical changes in the samples were monitored by IR spectroscopy during annealing.

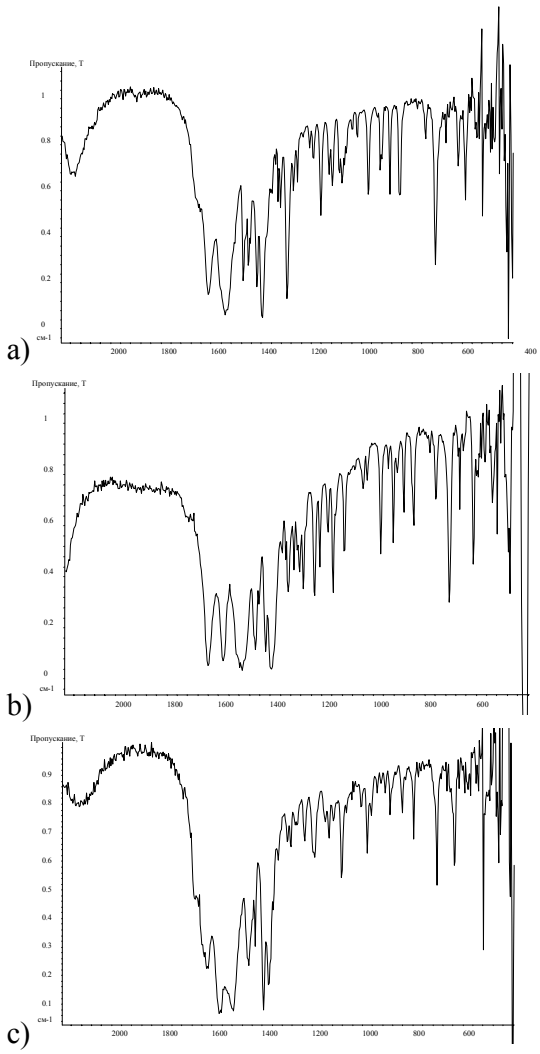

Fig. 1. Gabapentin FT-IR -spectra at 293 K (KBr).

In present work this method was successfully developed for chemically labile compound named gabapentine [1-(aminomethyl)-cyclohexaneacetic acid]. According data obtained by FT-IR, X-ray diffraction and DSK, the formation of three kinetically stable crystal polymorph modifications of gabapentine (Forms 1, 2 and 3) was observed. Form 1 is the commercial one (Fig. 1a). Form 2 is well known in literature (Fig. 1b) [1] was obtained at surface temperature 80K and form 3 is new one (Fig. 1c) at room temperature.

So, we have shown that properties of the samples obtained are highly depended upon surface temperature.

This work was supported by "Start" program.

Literature:

1. Patent WO 98/28255

Cryomodification of flucticasone propionate structure

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The development of new methods, which effected on physical and chemical properties of solid drug substances with the aim of improvement of their pharmaceutical and therapeutical characteristics, is a very actual task at the present time.

Dispersity of drug substances particles, their form, crystal structure, the combination of drug substances with additional components on molecular and supermolecular levels are the main factors determined pharmaceutical properties of medical preparates on their base.

We have proposed method, which is able to rise of physical and chemical and pharmaceutical properties of drug substances. It is based on the formation of non-equilibrium solid states of drug substances and additional components by sublimation and vapor condensation on cooled surfaces with consequent heating to required temperature.

The effectiveness of this approach have been illustrated on example of flucticasone propionate [6-α. 11-β, 16-α, 17-β) 6,9-difluoro-11-hydroxy-16-methyl-3-oxoandrosta-1,4-diene-17-propionyloxy-17-thiocarbonic acid – S-(fluoro-methyl) ester. This substance is devoted to steroid drugs and the results obtained are important for this drugs class.

The study of the new flucticasone propionate modifications was carried out under vacuum conditions or using nitrogen atmosphere at surface of condensation temperature varied from 77 upto 330 K. It was established that particle size decrease from 50-100 μm for the commercial product to 0,5-1 μm for cryomodified substance. The mentioned size can be considered as a higher limit determined by the resolution of optical microscope used. The samples dispersity characterized by the narrow size distribution (SPAN is 1-1,3), that is significantly better than for different methods used the solvents.

Rising the flucticasone propionate molecular flow on the cooled surface and growing the temperature of this surface led to the decrease of average particle size.

The analysis of IR-spectra and X-ray data showed that cryomodification changes the flucticasone propionate molecular packing. Depending upon molecular condensation flow rate and cooled surface temperature sample crystal structure remained the same or differed from the commercial product. In the last case we have succeeded in the formation of new flucticasone propionate crystal modification, which is metastable and is changed to the stable phase during two weeks at room temperature.

The results obtained during this work show the possibilities of low temperatures for the directed modification of solid drug substances structures. *Acknowledgements*. The work was financially supported by Russian Foundation of Basic Research grant 05-03-32293.

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Structural characterization of gold contained mono- and bimetallic catalysts, synthesized by metal vapor synthesis, by means of X-ray photoelectron spectroscopy

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Bimetallic Au-Ni nanoclusters, synthesized by metal vapor synthesis (MVS) with triethylamine, possess synergetic activity in catalytic hydrocarbon conversion [1]. Information on the Au and Ni chemical states and nature of interaction between Au and Ni in bimetallic nanoparticle are necessary for understanding Au-Ni synergetic properties. Thus the main goal of the present work is to establish Au and Ni chemical states in bimetallic nanoparticle by means of XPS.

In the present work mono- and bimetal nanoparticles M (M=Au, Ni, Au-Ni) were synthesized by MVS with triethylamine as described in [1] and immobilized on SiO_2. The supported nanoclusters activity was measured in allylbenzene isomerization as described in [1]. Gold and nickel chemical states were characterized by means of XPS. Nanoclusters structural, catalytic and spectral characteristics are presented in tables 1-2.

Table 1. Metal content in nanocomposites, synthesized by MVS with triethylamine, and nanocomposites catalytic activity [A]=[mol/mol*h] in allylbenzene isomerization at 170^0C.

Sample	Au-Ni/SiO_2	Au-Ni/SiO_2	Au-Ni/SiO_2	Ni/SiO_2	Au/SiO_2
Sample number	**1**	**2**	**3**	**4**	**5**
Au, weight %	0.14	0.40	0.45	-	0.21
Ni, weigh %	0.10	0.16	0.46	0.30	-
A, mol/mol*h	5583	4624	242	0	108

Table 2. Binding energy [E_b]=[eV] in Ni/SiO_2, Au/SiO_2, Au-Ni/SiO_2 XPS spectrums

Metal	E_b	Sample number				
		1	**2**	**3**	**4**	**5**
Ni	E_b, 2p3/2	856	856.7	856.9	855.9	-
Au	E_b, 4f7/2	84.3	84.2	84	-	84,0

Results and Conclusions:

- XPS spectrums (table.2) were compared with reference nickel and gold XPS spectrums described in [2]. It was revealed that the main nickel chemical state in all samples is NiO, the main gold chemical state - Au^0. The obtained results are discussed.
- The difference $\Delta=E_b$(Ni 2p3/2)-E_b(Au 4f7/2) in samples 1-3 described nickel-gold interactions. It was obtained, that the growth of this parameter (Δ) correlates with bimetallic activity (table 1-2). Thus, the discussed energy difference could serve as indicator of bimetallic composites activity in the catalytic hydrocarbon conversion.

This work was carried with financial support from the RFBR (grant 05-03-33065, 04-03-32311) and ISTC (project 2955).

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Kinetics of radiation-induced subthreshold defect formation in rare-gas solids

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Rare-gas solids (RGS) are the model systems in physics and chemistry of solids, and a lot of information about their electronic excitations has been documented in several books and reviews (see e.g. Ref. 1 and references therein). Because of strong interaction with phonons the excitons and holes in RGS are self-trapped, and a wide range of electronic excitations are created in samples: free excitons, atomic-like (A-STE) and molecular-like self-trapped excitons (M-STE), molecular-like self-trapped holes and electrons trapped at lattice imperfections. The trapping of electronic excitations induces inelastic modification of RGS crystal lattice [1]. The subthreshold inelastic radiation-induced atomic processes in RGS such as defect formation and desorption under excitation by photons and electrons with a kinetic energies below the threshold of knock-on of atoms from the lattice sites were studied recently [2]. Local elastic and inelastic lattice deformation around trapped electronic excitations, population of the antibonding electronic states during relaxation of the molecular-like centers, and excitation of the Rydberg states of guest species are the moving force of point defect formation in RGS. The coexistence of free and trapped excitations and, as a result, the presence of a wide range of luminescence bands in the emission spectra enable one to reveal the energy relaxation channels and to detect the elementary steps in lattice rearrangement. However, to our knowledge, the kinetic analysis of the dose curves of electronic excitation induced accumulation of crystal lattice imperfections in RGS was not done up to now.

In the present paper we propose the simple kinetic model for excitonically-induced defect accumulation processes, using photoluminescence as a sensitive tool for real-time monitoring of the point defect concentration in RGS under irradiation. The experiments were carried out at the SUPERLUMI-station at HASYLAB, DESY, Hamburg. The process of defect accumulation may be written as consecutive process $E + T \leftrightarrow S \rightarrow D$, where E is the mobile excitation (e.g. free exciton), which is trapped at trapping center T (e.g. lattice imperfection) and forms an excited metastable trapped center S (e.g. A-STE, or M-STE), which can be considered as metastable short-lived lattice defect. Radiative decay of the short-lived S-center either returns the lattice into the initial state without permanent defect, or forms the permanent defect D (Frenkel pair). The time dependence of luminescence intensity of 'defect' subband under steady-state conditions may be expressed in form: $I(t) = I_0 + (L + t)^{-1} \cdot K \cdot t$, where K and L are the specific constants expressed via the rate constants of elementary steps in the process; I_0 is the initial intensity of 'defect' luminescence due to preirradiated defects. The results of fitting of time dependences of radiation-induced changes in photoluminescence spectra of solid Xe and Ne will be presented.

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The structure and photochemistry of the hydrogen bonded complexes between nitrous acid and 1,1-dichloroethylene in argon matrices FTIR and theoretical study [1, 2]

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Vinylidene chloride is used industrially for the production of poly(vinyl dichloroethylene – PVDC) and is clasified as a possible human carcinogen (Integrated Risk Information System of EPA). The dichloroethylenes represents significant organochlorine emissions to the enviroment. Nitrous acid acts in atmosphere as a source of hydroxyl radicals. Molecular complexes formed between HONO and 1,1-$C_2H_2Cl_2$ and their photochemistry are of interest as they may play a key role in troposphere.

In the present work the complexes between trans- and cis isomers of nitrous acid and 1,1-dichloroethylene have been identified and photolysed in argon matrices. The experimental spectra proved the formation of two types of hydrogen bonded complexes, in which trans- and cis-HONO isomers act as proton donors. In the first type of the complexes, characterized by T-shaped structure, the interaction between OH group of HONO and π electrons of C=C bond occurs. The second type is characterized by O-H…Cl interaction.

The spectroscopic investigations were supported by MP2 calculations with 6-311++G(2d,2p) basis set. The theoretical studies indicate two stable structures for the HONO···1,1-$C_2H_2Cl_2$ complexes with OH…π hydrogen bond, which differ in orientation (perpendicular or parallel) of nitrous acid plane with respect to the C=C double bond. In the case of the O-H…Cl complexes, three stationary points were found on the potential energy surface. Two of them represent the planar or non-planar geometry with single O-H…Cl hydrogen bond. The third stable structure shows three-centered ("bifurcated") Cl…H(-O)…Cl hydrogen bond.

The HONO···1,1-$C_2H_2Cl_2$ complexes present in argon matrices were subjected to UV radiation (λ>340nm) from medium pressure mercury lamp. The products of the photolysis were detected by means of FTIR spectroscopy. Two conformers of 2-nitroso-2,2-dichloroethanol molecule have been identified as the final products of the double addition reaction of the OH, NO radicals to 1,1-dichloroethylene. The additional reactive species observed in the matrix was tentatively identified as 1,1-dichloro-2-hydroxyethyl radical, an intermediate formed by single addition of OH to 1,1-dichloroethylene. The identities of the products have been confirmed by the experiments with deuterated DONO, by concentration and annealing studies and by reference to the spectral data of related molecules. The results of the quantum mechanical calculations confirmed both the identities of the new molecules and mechanism of the photochemical reaction that take place in the matrix.

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Radical intermediates on halogenation of carbon nanomaterials at low temperatures

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One of the leading tendencies in chemistry of nanomaterials is their modification for obtaining new properties. Halogenation as one of efficient methods of modification is of great interest because both chlorine- and fluoro- derivatives should serve as molecular intermediates for further modification. Chemical transformations of the attached functional groups give the base for the creation of principally new spatial structures based on carbonic nanomaterials. Extremal reaction activity of nanomaterials in halogen and fluorination processes of fullerene C_{60}, single- and multi-wall nanotubes, nanofibres at 77-240 K were investigated in present work by ESR and IR-spectroscopy methods.

The fullerenes demonstrate inherent paramagnetizm in ESR spectra as narrow singlet line with width ΔH=0.2 mT and g=2,002, sometimes additional singlet at g=1.998 appears of these paramagnetic centers (PMC). The concentrations PMC for different fullerenes are $3x10^{17}$ – – $4x10^{15}$ spin/g. During the contact of C_{60} with molecular fluorine at 77 K new signal with ΔH=1,7 mT and g=2,0023 arises, another narrow slight signal can be seen in its central part. The new signal in the contrast to inherent PMC signal does not saturate even at microwave power as high as 5.0 mW and it can be reliably distinguished. The PMC density grows for the account of fluorination up to $3x10^{19}$ spin/g. The PMC thus obtained possess high stability besides both their number and spectrum shape do not change under heating to 373K. Chlorination of fullerene has been carried out by molecular and atomic chlorine. In ESR spectra of products obtained three types of singlet with different width and g-factor were distinguished: ΔH=0.35-1.5-2.7 mT; g=2.001-2.0016-2.000. These data are the evidence of generation of PMC with different number atomic chlorine attached to molecular conjugated system of fullerene. In dependence of chlorination conditions the PMC densities were $7x10^{16}$–$1.3x10^{18}$ spin/g (PMC background density was $4x10^{15}$ spin/g).

Gravimetric and elemental analysis lead to the following bruto-formula for the products of fullerene chlorination $C_{60}Cl_n$ (n=2÷8). The broad bands in IR spectra close to characteristic vibrations for C–Cl bonds (frequencies 885, 850 and 808 cm^{-1}) evidenced the presence of the mixture different isomers in the sample.The hydrocarbon chlorination reactions usually display the radical-chained character of their mechanisms. Such a mechanisms can be suggested as well for low temperature chlorination of carbon nanomaterials. The kinetic chain length in this process is as high $3x10^4$–10^6 (for chlorides of $C_{60}Cl_2$ and $C_{60}Cl_8$ compounds correspondingly).Elemental analysis of chlorinated samples of carbonic nanofibers and multiple wall nanotubes revealed that the abundance of chlorine in compounds obtained is 5,8 and 1,3 mass. %, respectively.

Thus, for the first time it is shown that carbonic nanomaterials (fullerene, single- and multiwall nanotubes, nanofibers) demonstrate high activity at cryogenic conditions (77K) in reactions of chain halogination (F_2, Cl_2) with kinetic chain length up to 10^4 –10^5. The ESR spectra of active free- radical intermediates were recorded. The presence of vibration bands of C–Cl bonds in products has been indicated by IR method. For the first time chain fluorination of carbonic nanofibers, mono- and multi-wall nanotubes have been performed at low temperatures.

The work was supported by the Russian Foundation for Basic Research (RFBR grant № 06-03-32898)

Concentration effect on the nuclear spin conversion of water in Ar matrix

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Water and other molecules of astrophysical interest like H_2, NH_2, or H_2CO, exist in two nuclear spin species. They are called *ortho* and *para* depending if the spins of the protons are parallel (total nuclear spin I=1) or anti-parallel (total nuclear spin I=0). In gas phase, each rotational state is associated with only one of the nuclear magnetic species and in the high temperature limit (>50 K), it is known that ¼ of the molecules are *para* while ¾ are *ortho*. Below 50 K, the ortho-to-para ratio becomes strongly temperature dependent. From the ortho-to-para abundance ratios of molecules measured in cometary *comae* [1, 2] or in dark clouds [3], it is expected to determine the formation conditions of molecules in space, and especially the formation temperature.

In this context, we have investigated the parameters involved in the nuclear spin conversion of water in rare gas solids at low temperatures. In this environment, the water molecule rotates almost freely and is able to perform translational oscillations within the cage made of rare gas atoms. We present here a study, in the mid-infrared, of H_2O in argon matrix between 4.2 and 30 K. The spectra were recorded in the frequency range 400-4000 cm^{-1} with resolutions of 0.15 and 0.03 cm^{-1} using a Bruker 113V FTIR spectrometer. In the vibrational ν_1, ν_2 and ν_3 regions of water, the spectrum exhibited several rovibrational lines weakly shifted from the gas phase ones. And besides these lines, it remained [4] at 6 K in the ν_2 bending mode, a wide structure attributed to the Coupling of the Rotation and the Translation (RTC) of the molecule within the cage.

After a fast cooling from 30 K to 4.2 K, populations of the two species *ortho* and *para* did not follow the Bolztmann distribution due to slow nuclear spin conversion. Following the time evolution of the transitions associated with the *ortho* and *para* species, we have measured characteristic times of nuclear spin conversion in various conditions. At 4.2 K in argon matrix, we observed an acceleration of the nuclear spin conversion as the concentration of water in the sample increased. Calculations performed by our group show clearly that intermolecular magnetic interactions are responsible for this concentration dependence. For more diluted samples, we measured a characteristic time of 700 minutes that can be attributed to magnetic intramolecular interactions. The measured time is however much longer than the one observed in solid parahydrogen. At 20 K, the measured times are much shorter and the concentration effect remains important. It is then surprising that characteristic times in cryogenic matrices are much shorter than months estimated in ice by Tikhonov and Volkov [5] at 77 K.

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Rotation of methyl radicals in solid argon matrix

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High-resolution electron spin resonance (ESR) measurements of methyl radicals in solid argon matrix were carried out in temperature range from 14 K to 35 K. The spectrum consists of two different species having either (I) symmetric (spin part anti-symmetric) or (II) anti-symmetric (spin part symmetric) rotational wavefunction [1]. The relative intensities of the (I) and (II) lines are strongly temperature dependent due to thermal population of the rotational states [2]. At the lowest temperatures, we have observed an ESR spectrum that corresponds to an axially symmetric species having both hyperfine and g anisotropy. The observed difference between A_{zz} and $A_{xx} = A_{yy}$ is 0.1 G, which corresponds exactly to the theoretical prediction [3]. This result shows that methyl radical rotates only around the C_3-axis but not around the C_2-axes below 15 K. Furthermore, the C_2-rotation can be thermally activated above 15 K. Additional evidence for the thermal activation of the C_2-rotation was obtained from measurements of spin-lattice relaxation time (T_1). Dependence of T_1 on temperature was strongly non-linear and considerably higher than below 4 K. Changes in T_1 occur in the same temperature range as the C_2-rotation became active. The isotropic hyperfine coupling constant for species (II) was strongly temperature dependent below 20 K. This is most likely also related to thermal activation of the C_2-rotation. No such dependence was observed for (I) lines.

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Matrix isolation and computational study of the photochemistry of *p*-azidoaniline

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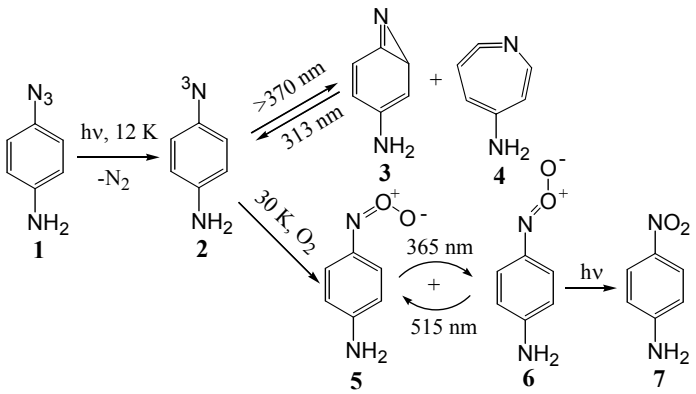
Photolysis of *p*-azidoaniline (**1**) – unlike that of phenyl azide and most of its derivatives – gives only products of triplet nitrene reactions [1, 2]. Since the early seventies it has been known that triplet arylnitrenes react with oxygen by formation of adducts [1, 3, 4]. In an early study on 1,4-diazidobenzene, two types of adducts (diamagnetic and paramagnetic) were detected in glassy matrices [3]. It was proposed that the diamagnetic adduct is an arylnitroso oxide, R–N=O^+–O^-, and the paramagnetic species is the triplet aryliminodioxy diradical [3]. Subsequent studies did not confirm formation of triplet adducts [1, 4].

This investigation was devoted to experimental and computational study of the reactions of triplet arylnitrenes with oxygen in order to unambiguously identify the nature of intermediates and to understand their properties.

Before studying the reaction of triplet *p*-aminophenylnitrene (**2**) with O_2, we photolyzed **1** in an Ar matrix in the absence of O_2. Photolysis of **1** gives rise to **2** and keteneimine (**4**,1879 cm^{-1}). Formation of **4** during the decomposition of **1** in Ar is due to the secondary photolysis of **2**. According to the IR spectral data 80 % of **2** is formed after complete decomposition of **1**. The bleaching of **2** does not only give rise to **4** but also to azirine (**3**, 1710 cm^{-1}). Following irradiation at 313 nm leads to the partial re-formation of **2** from **3**. The electronic absorption spectrum of **2** is well reproduced by CASSCF/CASPT2.



Photolysis of **1** in an Ar matrix containing 4 % of oxygen leads to **2** and **4** also. Subsequent annealing of the matrix at 30 K allows for slow diffusion of O_2 and its reaction with **2,** which manifests itself in the growth of an intense absorption in the visible region. Earlier [1] we tentatively proposed the formation of two isomers: c*is*- and *trans*-*p*-aminophenylnitroso oxides (**5**,**6**) in glassy matrices at 77 K. Now with the help of quantum chemical calculations we were able to characterize **5** and **6**. Also we found no evidence for the triplet products resulting from the reaction of **2** with O_2.

We demonstrated that **5**, **6** can be interconverted by selective irradiation and that they are ultimately converted into *p*-nitroaniline (**7**). It has been proposed [3] that the photochemical formation of nitro compounds from nitroso oxides proceeds via intermediate dioxaziridines. Formation of such species was observed in glassy matrices at 77 K [4]. We were unable to detect the formation of the dioxaziridines on photolysis of **5**, **6** in Ar matrices at 12 K.

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Photochemical isomerization of highly symmetrical N_4S_4 in argon matrix

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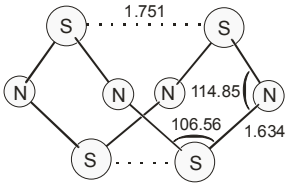
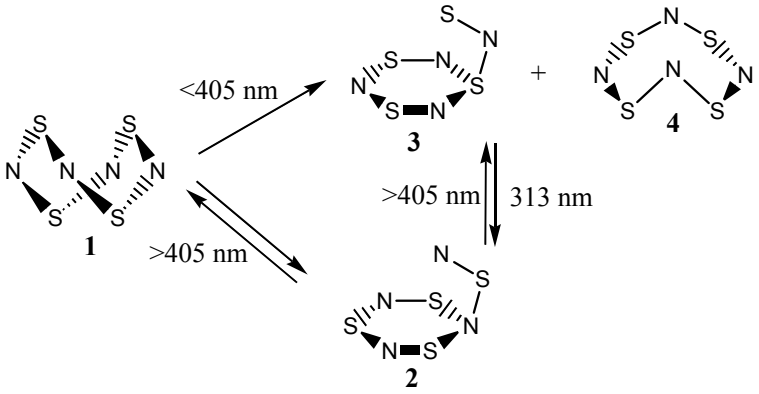
Over the last decade, a novel family of sulfur-nitrogen heteroaromatic and antiaromatic structures has been synthesized [1]. A unique feature of some of these compounds, as was revealed by our recent study [2,3], is the formation of stable π-radicals on their photolysis and mild thermolysis. In all cases, the primary processes were found to be the dissociation of a weak SN bond. To understand how typical this mechanism is for the photochemical transformations of polysulfur-nitrogen heterocycles, we investigated the photolysis of the simplest polysulfur-nitrogen heterocycle, S_4N_4 (**1**), a highly symmetrical species belonging to the D_{2d} point group.

Photolysis of **1** at room temperature did not result in any radical products. Photolysis of **1** in an argon matrix at 12 K leads to the formation of at least three products being the isomers of starting compound **1** (Scheme). UV-Vis and IR spectra of these products were recorded and assigned on the basis of CASSCF/CASPT2 and B3LYP calculations. Detailed analysis of the experimantal and computational results will be presented.

With selective irradiation, products **2**-**4** can be mutually interconverted as well as converted into the starting compound **1** (Scheme). Therefore, similar to the case of other investigated polysulfur-nitrogen heterocycles the primary process in the S_4N_4 photolysis is the cleavage of an SN-bond and the formation of a series of isomers.



D_{2d}



Scheme

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Keto-Iminol Tautomerism in Acetohydroxamic and Formohydroxamic Acids. Matrix Isolation and Theoretical Study

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Full Xe arc irradiation of acetohydroxamic acid (AHA) isolated in argon matrixes was used to study the keto-iminol tautomerism of this molecule. The energies and spectra of the most stable tautomers were simulated by *ab initio* calculations at the MP2 level using the 6-311++G(2d,2p) basis set.

The UV excitation leads to a strong decrease of the bands due to the most stable *cis* keto (1Z) AHA tautomer whereas some weak absorptions present in the spectra slowly reduce their intensities and a set of bands grow up. The comparison of the frequencies of these three sets of absorptions with the experimental frequencies of the 1Z structure as well as the calculated frequencies for the keto and iminol tautomers provide strong evidence for assignment of the weak bands decreasing after matrix irradiation to *cis* iminol (2Z) AHA and the bands growing after photolysis to *trans* keto (1E) AHA tautomer. Data obtained from the matrix spectra indicate that at 298 K the 2Z/1Z and 1E/1Z populations in the gas phase are about 0.039 ± 0.008 and 0.013 ± 0.005, respectively. The results of calculations are in accord with the experimentally determined order of stability of the AHA tautomers. The calculated stabilization energies of AHA structures (ΔE_{ZPE}) indicate that 1Z is 1.31, 1.35, and 5.75 kcal mol^{-1} more stable than the 2Z, 1E, and 2E tautomers, respectively. The differences of the Gibbs free energies ($\Delta G_{298.15}$) between the tautomers are very close to the ΔE_{ZPE} values and the theoretical relative abundances of the studied structures calculated from the Gibbs free energies at 298.15 K are: 87%, 8.6%, 4.4%, and 0.03% for the 1Z, 2Z, 1E and 2E tautomers of AHA, respectively.

The identification of the iminol (2Z) tautomer of acetohydroxamic acid inclined us to re-examine the FHA/Ar spectra obtained after matrix deposition and irradiation with Xe arc lamp, that were reported earlier [1]. A detailed comparison of the absorptions of both AHA and FHA acids enabled us to attribute a set of weak unassigned bands in the spectra of formohydroxamic acid to 2Z tautomer of FHA. The matrix spectra indicate that in the gas phase at room temperature the 2Z/1Z and 1E/1Z populations are about 0.027 ± 0.004 and 0.033 ± 0.014 for formohydroxamic acid, respectively. The calculations of the ΔE_{ZPE} energy differences show that 1Z FHA tautomer is 1.43, 1.25, and 5.29 kcal mol^{-1} more stable than the 2Z, 1E, and 2E structures, respectively. The theoretical relative abundances of FHA tautomers calculated from the Gibbs free energies at 298.15 K are: 77.6%, 9.4%, 13%, and 0.01% for 1Z, 2Z, 1E and 2E tautomers, respectively.

The obtained results clearly show that the methyl substituent at the carbon atom of hydroxamic acids changes the order of stability of the 2Z and 1E tautomers and the iminol form becomes more preferred structure.

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Modeling guanosine triphosphate hydrolysis by the Ras protein by QM/MM simulations based on the X-ray structure for the frozen GTP-Ras complex

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The hydrolysis reaction of guanosine triphosphate (GTP) by $p21^{ras}$ (Ras) has been modeled by using the *ab initio* type quantum mechanical – molecular mechanical (QM/MM) simulations. The initial positions of the atoms of the Ras-GTP complex were prompted by the crystal structure 1QRA from the Protein Data Bank. It was determined at the 1.6 Å resolution for the complex formed between $p21^{ras}$ and GTP using a combination of photolysis of an inactive GTP precursor and rapid freezing at 100K.

Simulations included scans of the composite multidimensional QM/MM potential energy surface in the regions where chemical bonds or hydrogen bonds could be cleaved or formed. As a result, the basins around presumable stationary points were specified for more careful calculations of the local minima or saddle points. All stationary points were located by unconstrained minimizations (for local minima) or by constrained minimizations (for saddle points) of the QM/MM energy. Locations of the saddle points or, in other words, of transition states (TS) were performed basing on the following criterion: the gradient of the constrained internal coordinate along an assumed reaction path must change its sign at this point. The polarized "LANL2DZdp ECP" basis set (and the corresponding pseudopotential for phosphorus) was used for all atoms except magnesium. For the latter, the standard 6-31 basis set was employed. The SCF approximation in the QM part and the AMBER force field parameters were applied in simulations.

It is shown that the minimum energy reaction path is consistent with a primarily dissociative type mechanism of GTP hydrolysis. At the first stage, a unified action of the nearest residues of Ras and the nearest water molecules results in a substantial spatial separation of the γ-phosphate group of GTP from the rest of the molecule (GDP). This phase of hydrolysis process proceeds through the low barrier (16.7 kcal/mol) transition state TS1. At the second stage, the inorganic phosphate is formed in consequence of proton transfers mediated by two water molecules and assisted by the Gln61 residue from Ras. The highest transition state at this segment, TS3, is estimated to have an energy 7.5 kcal/mol above the enzyme-substrate complex. Conclusions of the modeling lead to a better understanding of the anticatalytic effect of cancer causing mutation of Gln61 from Ras, which has been debated in recent years.

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Complexes of 1-methyl-uracil with metal chlorides in low temperature inert matrices

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The complexes of 1-methyl-uracil with different metal chlorides (sodium, nickel, and copper chlorides) were obtained by simultaneous evaporating and trapping in the low temperature Ar matrices at 12 K. For the simultaneous evaporation of thermounstable DNA fragments (1-methyl-uracil) and substances with high evaporation temperature the Knudsen cell with biomolecules was placed in line with the evaporation cell for metals. The matrix-to-substance ratio (M/S) was fixed by using the low temperature differential quartz crystal microbalance. In these experiments M/S for complexes (metal chlorides:1-methyl-uracil:Ar) were about 3:1:200. The FTIR spectra were investigated in the ranges 4000-400 cm^{-1} with KBr and CaF_2 beamsplitter and apodized resolution 0.4 cm^{-1}.

Common feature of all complexes was the emergence of additional absorption in the region of the stretching vibrations ν(C=O). For example, the new bands at 1694 cm^{-1} and 1690 cm^{-1} were detected in the spectra of complexes with sodium chlorides and copper chlorides respectively. It should be noted that, unlike sodium and nickel salts, the copper chlorides were in the form of trimer. The distinctive property of complexes with copper chlorides was a drastic decrease of the intensity of 1-methyl-uracil band 1650 cm^{-1}. After annealing of the matrix sample this band disappeared completely. It was a good correlation between the behavior of the bands 1650 cm^{-1} and 748 cm^{-1}. The band 748 cm^{-1} has an unambiguous assignment to the ring vibrations (νC4C5, νC5C6, νC6C1 according the calculation). Owing to this correlation the band 1650 cm^{-1} can also be assigned to C5=C6 bond of the pyrimidine ring. The nature of 1636 cm^{-1} band may be explained by Fermi resonance with C=O groups. The dramatic changes of C5=C6 band may be a marked property of complexes with coordination bonds between copper and C5, C6. Unlike complexes with copper, strong changes of the bands of 1-methyl-uracil 1650 cm^{-1} and 748 cm^{-1} were not registered in the spectra of complexes of sodium or nickel chlorides.

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Investigation of free radicals at low temperature radiolysis of substances exhibiting antimutagenic activity

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In connection with the global radioactive environmental pollution the problem of creation of substances capable of decreasing the level of cell genetic damage (i.e., reduce the risk of cancer) caused by gamma-irradiation has become more urgent.

The authors developed the approaches to construction of highly efficient antimutagenic systems based on polycations both of synthetic (diallyldimethylammonium series) and natural origin (chitosan and its derivatives). To realise the possible mechanism of such system protective action, and also to compare the substance radiation resistance and its antimutagenic efficiency the investigation of the free radicals generated at low-temperature (77K) radiolysis of polycations has been carried out via ESR spectroscopy method.

It was shown, that introduction of a relatively low amount (2 % mol) of GA fragments in the polymer structure resulted in the radioactive stabilization of a macromolecule. This was proved by decreasing of radical formation at an irradiation that correlated with the antimutagenic activity elevation for polycations bearing GA fragments in a polymer side chain. It is necessary to note, that at polymeric gallates radiolysis the stable (up to 300-400K) macroradicals of phenoxylic and semiquinonic type were obtained. This phenomenon confirms the expedience of such target polycation modification.

An introduction of GA-fragments (2-3 % mass) into the polymer side chain decreases substantially the radiochemical yield of PMCs. The results obtained allow us to explain the enhancement in antimutagenic activity of the polycations bearing GA-fragments.

The radical intermediates have been analyzed via ESR method. It was established that on the synthetic polycations radiolysis the primary free radicals were formatted mainly on the pyrrolidinium cycle of a polymer structure; in the case of natural polycations (CH, QCH) those were stabilized on the pyranose cycle of the polysaccharide chain.

The processes of the further thermo-conversion of the radicals obtained were accompanied by the dehydrogenation of C-H bonds and dehydration of the primary macroradicals (with an liberation of low molecular products) and formation of polyconjugated systems in macromolecules as a result of it. An analysis of the data obtained allowed us to realize the chemical nature of radical and ion processes taking place in polymers and permitted to develop the approaches to selection of biological active compounds for target synthesis of effective antimutagens and optimization of their composition.

Modification of fullerite C_{60} by cryochemical method

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The stable high-temperature phase of fullerite C_{60} is well-known to have the face-centered cubic (f.c.c.) structure. A fullerite phase with hexagonal close-packed structure (h.c.p.) has also been reported, however, it was found to be metastable to the f.c.c. phase. In general h.c.p. phase exists as an admixture in stable f.c.c.-fullerite. "New" h.c.p. phase may be perspective for photo-polymerization, intercalation and thermobaric treatment leading to new modified phases.

Previously [1] we suggested a cryochemical method to synthesize h.c.p. fullerite. The cryosynthesis involves three stages: (1) the rapid cooling of saturated solution of C_{60} in benzene with liquid nitrogen leading to the formation of so-called cryogranules; (2) the extraction, when the solidified benzene was removed at 255 K with *n*-hexane; (3) thermolysis of obtained clathrate in vacuum (10^{-2} torr) at 750 K for 7-8 h. The content of h.c.p. phase in the samples obtained was estimated to be 90–95%. It is significant that samples of h.c.p. phase also may be formed by methods of precipitation from saturated solutions or by cryochemical procedure with sublimation [2]. Only *n*-hexane leads to formation of h.c.p-fullerite C_{60} in the case of all three methods. Any other extractants/agents didn't allow to obtain h.c.p. phase.

The main aim of this work was to study the formation of h.c.p.-fullerite during cryosynthesis. X-Ray diffraction analysis and thermogravimetry were applied for characterization of the samples. Consequently, we studied all three stages of cryosynthesis:

Fullerene is found to be XRD-amorphous in cryogranules.

The formation of hexagonal packing motives of fullerite begins in the stage of extraction as clathrate with *n*-hexane (precursor of h.c.p.-fullerite). Its cell-parameters are defined. Model of structure is suggested. In this stage co-intercalation of CO_2 may also be realized.

H.c.p.-fullerite C_{60} is formed in the stage of thermolysis in vacuum after volatizing *n*-hexane at 100° C. Further heating lead to complete crystallization and removal of CO_2.

We also revealed that percentage of h.c.p. phase in final samples depends on size of cryogranules and temperature of *n*-hexane. It was studied that h.c.p.-precursors (clathrates) are stable on air, but transform to f.c.c.-fullerite at shear deformation.

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Gel-like phase of N_2O condensates

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There is an interesting aspect in the problem of nanostructured materials. A theoretical analysis [1] of the nucleation behavior of polar substances predicted the formation of a whole variety of clusters: linear chains, branched-chains and ring "polymers" during the condensation process. The particles are found [2] to associate to form chains of dipoles aligning "head-to-tail". According experimental data [3] in the supersaturated vapor polar molecules may be sufficiently associated. In this case the vapor is composed of individual molecules and of small, relatively stable, complexes. The homogeneous gas-liquid nucleation in this system is initiated by chainlike clusters .The system may form a "glassy" structure with chains that percolated [4]. An interpenetrating network of uncollapsed dipolar chain clusters is a model of gel-like phase according to [1]. To investigate the polar substance a convenient model object is solid N_2O. This molecular crystal consists of asymmetric linear molecules having the dipole moment. The structure of solid nitrous oxide is described by the ***Pa3*** space group, i.e. the molecular axes and their dipole moments are directed along the (111) cube diagonals.

Investigations were carried out by transmission electron diffraction using a helium cryostat. The specimens were prepared directly *in situ* by depositing the 99.99% pure gas simultaneously on the amorphous carbon and polycrystalline Al substrates. The condensation was realized at the substrate temperature 3.4 K. The gas was previously cooled in a condensation coil passing through a vessel containing liquid nitrogen. The electron diffraction technique was capable of detecting short-lived states and it was important for the investigation of the growth process, phase transitions.

The condensation of cooled N_2O gas led to formation of an anomalous state of the deposits. After the sample preparation an amorphous or ultradisperse phase was observed. This state of the condensates is very different from that of a typical "simple" amorphous phase. An unusual character became apparent during an annealing process. Heating the samples above 11-12 K caused the surprising transformation, which led to an appearance of large crystallites having hexagonal lattice. The new ***hcp*** phase was stable up to 30 K, then the crystallites collapsed. This change had an irreversible character. Subsequent cooling down to helium temperature could not reconstruct the primary state. The study has been carried out for the CO_2 condensates at the same conditions as N_2O samples in order to compare the results. As a molecule, CO_2 is physically very similar to N_2O, except for its dipole moment. The results obtained confirm that the presence of the dipole moment is the important factor for the formation of this "glassy" state.

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Theoretical prediction of noble-gas compounds Ng-Pt-Ng (Ng = Ar, Kr, Xe)

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Ab initio theoretical calculations play the significant role in recent progresses of noble gas (Ng) chemistry. In the present study, we have investigated the binding of Ng atoms (Ng = Ar, Kr, Xe) with Pt atom by the spin-restricted RCCSD(T) method in which inner-shell orbitals were frozen for noble gas atoms, while the excitation from 5*s*, 5*p*, 5*d*, and 6*s* orbitals were taken into account explicitly for Pt atom. The relativistic effects were included by using the Douglas-Kroll relativistic one-electron integrals with the relativistic basis sets by Tsuchiya et al. In the estimation of the interaction energy between Pt and Ng atoms, the basis set superposition error was corrected by the counterpoise correction method. We also calculated potential energy curves for the low-lying triplet states of Pt-Ng and Ng-Pt-Ng, which correlate to the triplet ground state of Pt (^{3}D). It is shown that two Ng atoms can bind with Pt atom in linear geometry in the singlet lowest state where the second Ng atom attaches to Pt with the larger binding energy than the first Ng atom. The binding energy is evaluated as 8.2, 17.9, and 33.4 kcal/mol for Ar-Pt-Ar, Kr-Pt-Kr, and Xe-Pt-Xe, respectively, relative to the triplet ground state of the dissociation limit, Pt (^{3}D) + 2Ng. The present results indicate that these Ng-Pt-Ng compounds are possible new gas-phase or matrix species.

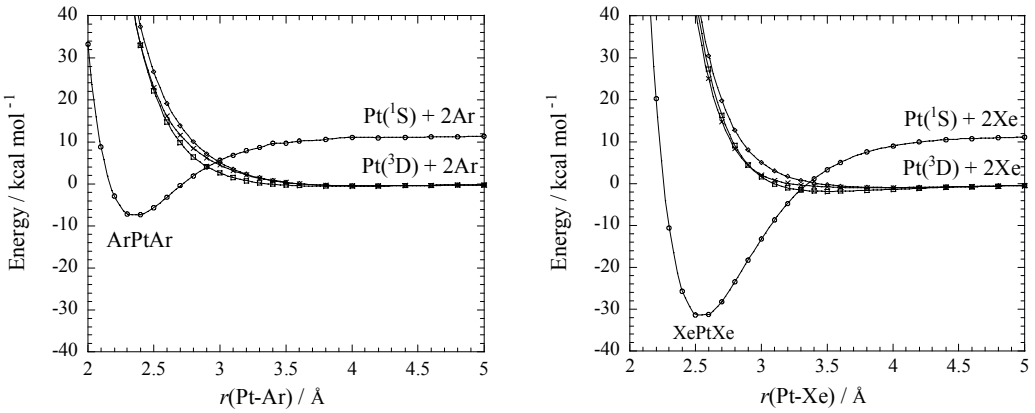

Figure 1. Potential energy curves for the lowest singlet ($^1\Sigma^+$) and triplet ($^3\Sigma$, $^3\Pi$, $^3\Delta$) states of Ng-Pt-Ng (Ng = Ar, Xe) as a function of Pt-Ng distance, r(PtNg).

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Cryoformation of copper atom cyanobiphenyl complexes and nanoclusters and their reactions with carbon tetrachloride

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Triple copper-carbon tetrachloride-4-pentyl-4-cyanobiphenyl (CB) films were obtained by vacuum deposition of component's vapors on the quartz surface under vacuum using molecular beam conditions at 80K. Copper vapor was produced by resistive heating of copper droplet in quartz evaporator at 1520 K, cyanobiphenyl component was evaporated at 400K. Carbon tetrachloride vapor was introduced in the system by needle-leak vessel with solid CCl_4 at 160K. After co-condensation the samples were investigated by ESR spectroscopy at of 80K and by heating in temperature range 80-350K, maintained by gas-flow cryostat.

The ESR spectra of these samples consist of two overlapping signals - the Lorentz singlet with approximately 10G width due to copper nanoclusters and complicated quartet signal due to complex of copper and cyanobiphenyl formation. The relative intensities of these signals vary with copper abundance. The more copper in system the more intensive singlet signal.

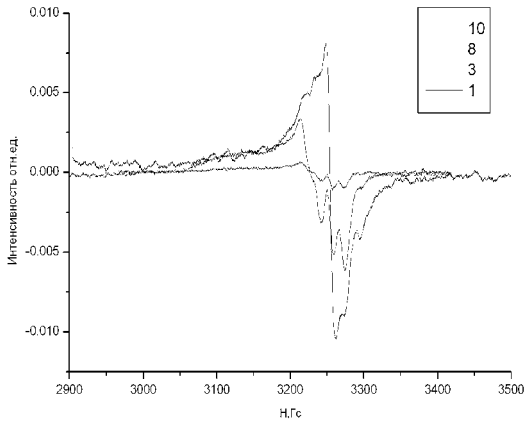

Fig. 1. ESR spectra of copper-cyanobyphenyl cocondensate with differ copper content(mol. % of Cu) at 80 K.

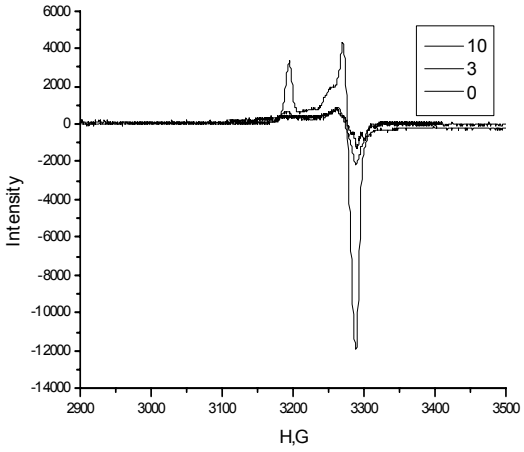

Fig. 2. ESR spectra of triple copper-cyanobyphenyl-CCl4 cocondensates with differrent copper content(mol. % of CCl4).

Introducing the rising amount of the third active electron acceptor compound carbon tetrachloride with components ratio ($Cu:CCl_4$:5CB=1:1:100 to 1:10:100) of carbon tetrachloride in the sample led to vanish of quartet lines in resulting spectra due to reaction of copper atoms with CCl_4, taking place during co-condensation process at 80 K, the intensity of singlet feature in spectrum remained unaffected.

Heating of the sample, containing no CCl_4 from 80K to 300 K led to decrease of intensity of quartet signal and simultaneously increase of intensity of singlet. Such changes in spectra resulted of aggregation process of copper atoms realized from copper-cyanobiphenyl complexes, which undergo decomposition at 120-150K. Heating of the sample with CCl_4 led only to change the shape of the singlet signal, which became more symmetric and narrow. So, the process of the interaction of mostly active copper clusters with CCl4 effectively tool place and copper cluster's size distribution changes and becomes narrower due to maintaining of less reactive clusters. The presence of carbon tetrachloride in copper-cyanobiphenyl co-condensate were suppress the complex accumulation in sample, possibly due to reaction between copper atoms and their complexes with carbon tetrachloride.

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Raman-spectrum of nitrogen-helium solid

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Raman spectroscopy has been used to investigate the structure and thermal stability of the nitrogen-helium solid. The spectra are similar with the spectra of bulk nitrogen indicating ordered structure inside cluster. The structure of the solid is shown to be dependent on the concentration of impurity in the sample preparation gas mixture more diluted mixtures yielding less dense solids. In most dilute samples evidence of disordered nitrogen on surface of the clusters is also detected. Macroscopic changes in structure are visually observed as function of impurity concentration. Removing the superfluid and annealing the sample makes the solid to collapse into approximately ten times more dense form at approximately 13 K. The α-solid – β-solid transition was seen in collapsed nitrogen sample approximately at the same temperature as in solid nitrogen film evidenced by the ~0.8 cm^{-1} shift in the peak position.

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New approach to the experimental measurement of van der Waals binding energy in small clusters

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The experimental measurement of the strengths of van der Waals bonds is a significant problem nowadays.

In the present study the new approach to this problem is developed. The main idea of the approach is to measure the kinetic energies of all products arising in the photodissociation of the cluster. The strength of van der Waals bond then can be calculated with using of the energy conservation equation.

The developed approach has been applied to the experiments on the photodissociation of T-shaped clusters O_2-Xe, O_2-CH_3I, and O_2-C_6H_{12}. The kinetic energy of the fragments has been measured with using of the velocity map imaging technique.

The values of van der Waals binding energy obtained in those experiments are in a good agreement with the existing experimental data and with the results of the quantum chemical calculations for the complexes under study.

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Low temperature complexes of samarium and europium with substituted cyanophenyls

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Metastable complexes of samarium and europium with mesogenic 4-penthyl-4'-cyanobiphenyl (5CB) and 4-penthyl-4'-cyanophenylpyridine (5Py) were produced by low temperature co-condensation of reagents vapor in our previous works [1, 2]. The complexes have been investigated in argon and ligand matrices in the temperature range 6-10 and 80-300 K. Stoichiometric mole metal/ligand ratio in these complexes is 1:2 (complex I, IR band 2135 (5CB), 2150 cm^{-1}(5Py)) and 1:1 (complex II, IR band 2085(5CB), 2100 cm^{-1}(5Py)).

The optimization of geometry has been carried out for europium atom and dimer complexes. Calculations have been made at DFT level with the exchange-correlating potential B3LYP using NWCHEM program [3]. Optimized structures have the sandwich-like structure and include one or two europium atoms between aromatic rings of two ligand molecules. Basic electronic states have multiplicity equal 10 and 15 for the complexes EuL_2 and Eu_2L_2 respectively. The estimation of frequencies of C≡N stretching vibrations in the complexes has confirmed red-shift of this band due to the complex formation.

The co-condensates Sm(Eu)/5CB(5Py) contain complex ML_2 firmed at the temperature 80 K. Annealing to the temperature 170-210 K leads to disappearance of ML_2 and appearance of complex M_2L_2. Suggested scheme of transformations includes the decomposition of the complex 1:2 and formation of the complex M_2L_2 by the reaction of metal atom with ML_2, decomposition of the complex 2:2 and metal aggregation, forming nanosized metal clusters stabilized in matrix.

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Ab initio MP2 and FTIR matrix isolation studies of complexes formed between nitric oxide dimer and water

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Owing to its importance in both atmospheric and biological studies the nitric oxide dimer $(NO)_2$ has been extensively studied with various experimental and theoretical methods. Several structures of the NO dimer have been recognized corresponding to a planar configuration and it is now well established that the most stable geometry corresponds to the cis ON-NO form.

In this contribution we present and discuss results of FTIR studies obtained for complexes formed between cis-$(NO)_2$ and water isolated in low temperature matrices. The interaction between these species leads to perturbation of both $(NO)_2$ and H_2O molecules as indicated by new features observed in the infrared spectra.

The strength of interaction, vibrational properties and possible structure of the complexes formed have been studied by means of MP2/6-311++G(2d,2p) method. Four minima have been found at this level of theory for cis-$(NO)_2$-H_2O complex with the binding energy less than -3 kcal/mol. All are hydrogen bonded species with water molecule acting as a proton donor but they differ by the site of interaction. In two more stable structures O-H group interacts with one or two N atoms of $(NO)_2$ while in two less stable complexes one or two O atoms of $(NO)_2$ are proton acceptor sites. Comparison of the calculated frequencies with those observed for $(NO)_2/H_2O$/Ar matrices indicates that the most stable complex with the O-H group of water molecule attached to two nitrogen atoms of $(NO)_2$ dimer is trapped in the studied matrices.

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