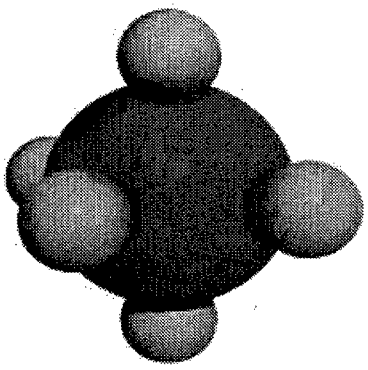
The Eighteenth Colloquium on High Resolution Molecular Spectroscopy

DIJON 2003

8–12 September 2003

Université de Bourgogne

DIJON – FRANCE



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14. ABSTRACT

The Book of Abstracts for 18th International Colloquium on High Resolution Molecular Spectroscopy, 8 September 2003 - 12 September 2003

This is an interdisciplinary conference. The program covers the following fundamental and applied spectroscopic themes: Rotational, Infrared, Electronic, Dynamics, Atmospheric, Astrophysics, Theory, Novel techniques and Diagnostics.

15. SUBJECT TERMS

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The Eigtheenth Colloquium on High Resolution Molecular Spectroscopy

DIJON 2003

8–12 September 2003

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DIJON 2003 – COLLOQUIUM PROGRAM

DATES	**08/09/2003**	**09/09/2003**	**10/09/2003**	**11/09/2003**	**12/09/2003**
Hours	Monday	Tuesday	Wednesday	Thursday	Friday
9:00 **11:00 – 12:30**	**Inv. speakers** **A** + Poster Session B	**Inv. speakers** **E** + Poster Session F	**Inv. speakers** **I** + Poster Session J	**Inv. speakers** **K** + Poster Session L	**Inv. speakers** **N** + Poster Session O
	Lunch†	Lunch†	Lunch†	Lunch†	Lunch†
14:00 **16:00 – 17:30**	**Inv. speakers** **C** + Poster session D	**Inv. speakers** **G** + Poster session H	*Departure 13:00* **Sight seeing tour**	**Free afternoon**	**Inv. speakers** **P**
	Dinner†	**Town Hall reception**		Dinner†	
Evening			**Banquet**	Poster session M	

† **Please note :** There will be free access to the restaurant from **12:30 to 13:15 (restaurant closed at 14:00) for lunch** and **from 18:30 to 19:30 for dinner**.

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Program of Sessions

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Invited Lectures A, Monday, September 8, 9:00

Chairman : M. QUACK

A1 – *QUANTITATIVE ROTATIONAL SPECTROSCOPY FOR ATMOSPHERIC RESEARCH (45 min.)*
G. WLODARCZAK

A2 – *NEW FRONTIERS IN LASER SPECTROSCOPY (45 min.)*
T. W. HÄNSCH

Poster Session B, Monday, September 8, 11:00

B1 – *ANALYSIS OF PHOSPHINE IN THE 3 μm REGION FOR PLANETARY APPLICATIONS*
L. SAGUI, I.KLEINER, R. A. H. BUTLER and L. R. BROWN

B2 – *SIMPLE, HIGHLY-MODULAR, MULTI-PLATFORM COMPUTER TOOLS FOR THE SIMULATION AND ANALYSIS OF HIGH-RESOLUTION RADIO-ASTRONOMICAL SPECTRA*
A. KLOTZ, A. WALTERS, E. CAUX, J. CROVISIER

B3 – *ABSORPTION SPECTROSCOPY OF JET-COOLED PAHS*
O. SUKHORUKOV, A. STAICU, and G. ROUILLÉ, F. HUISKEN and T. HENNING

B4 – *ONE MARTIAN YEAR OF THE ORBITING THERMAL EMISSION SPECTROMETER'S OBSERVATIONS OF THE 10μm CO_2 HOT BAND EMISSION*
W.C. MAGUIRE, J.C. PEARL AND M.D. SMITH, B.J. CONRATH, A.A. KUTEPOV, P.R. CHRISTENSEN

B5 – *CH_2CN^-: CARRIER OF THE 8037 Å DIFFUSE INTERSTELLAR BAND?*
M. A. CORDINER, P. J. SARRE

B6 – *TiO AND VO IN STELLAR AND CIRCUMSTELLAR ENVIRONMENTS*
R. HUNTER, P. A. COUCH, J. McCOMBIE and P. J. SARRE

B7 – *SUB-DOPPLER SPECTROSCOPY OF HYDROGEN AND DEUTERIUM CYANIDE ISOTOPOMERS*
S. BRUENKEN, V. AHRENS, U. FUCHS, S. THORWIRTH, F. LEWEN, G. WINNEWISSER, MARIE SIMECKOVA AND STEPAN URBAN

B8 – *OPTICAL PARAMETRICAL OSCILLATORS - A NEW LIGHT SOURCE FOR HIGH RESOLUTION SPECTROSCOPY*
ANDREAS HECKER, MARTINA HAVENITH

B9 – *DOPPLER-FREE TWO-PHOTON FLUORESCENCE EXCITATION SPECTROSCOPY AND THE ZEEMAN EFFECT OF THE 14_0^1 AND $14_0^1 1_0^1$ BANDS OF THE C_6D_6 $\tilde{A}\ ^1B_{2u} \leftarrow \tilde{X}\ ^1A_{1g}$ TRANSITION*
J. WANG, M. MISONO, S. KASAHARA, and HAJIME KATÔ , M. BABA

B10 – *DOPPLER-FREE POLARIZATION LABELING SPECTROSCOPY OF NAPHTHALENE MOLECULE*
SHUNJI KASAHARA, MD. HUMAYUN KABIR, YOSHIO TATAMITANI, HAJIME KATÔ, MASAAKI BABA

B11 – *BROADBAND KILOMETRIC ABSORPTION PATH LENGTH SPECTRA IN THE 1.5 μm REGION*
F. GUEYE, G. GUELACHVILI, N. PICQUÉ, M. CHENEVIER, E. SAFARI

B12 – *HIGH-RESOLUTION LASER PHOTOACOUSTIC SPECTROSCOPY OF PH_3: THE FIFTH P-H STRETCHING OVERTONE BANDS*
T.R. HUET,F. HERREGODTS, W. JERZEMBECK, and I. KLEINER

B13 – *TRANSITION INTENSITIES IN H_3^+ AND ISOTOPOMERS*
JAYESH RAMANLAL, OLEG POLYANSKY and JONATHAN TENNYSON

B14 – *ACETYLENE AS A HYDROGEN BOND DONOR: VIBRATIONAL SPECTRA AND DYNAMICS OF ISOLATED CLUSTERS*
Y. LIU, P. BOTSCHWINA, M. SUHM

B15 – *A NOVEL APPROACH TO THE ANALYSIS OF THE RYDBERG SPECTRA OF HCO*
SARAH J. BROWNBILL, TIMOTHY P. SOFTLEY

B16 – *ISOTOPE EFFECTS AND BORN OPPENHEIMER BREAKDOWN IN EXCITED SINGLET STATES OF THE LITHIUM DIMER*
A. ADOHI-KROU, F. MARTIN, A. J. ROSS, C. LINTON, and R. J. LE ROY

B17 – *LATTICIES OF QUANTUM NUMBERS AND THEIR DEFECTS*
B. ZHILINSKII

B18 – *QUALITATIVE ANALYSIS OF CENTRIFUGAL EFFECTS IN ROTATIONAL SPECTRA OF NEARLY SYMMETRIC TOPS*
BORIS ZHILINSKII, EVGENY SINITSYN

B19 – *A NEW SCHEME OF K-LABELING FOR TORSION-ROTATION ENERGY LEVELS IN LOW-BARRIER MOLECULES*
V.V. ILYUSHYN

B20 – *MILLIMETER-WAVE SPECTRUM AND GROUND STATE CONSTANTS OF METHYLAMINE*
V. V. ILYUSHYN, E. A. ALEKSEEV, S. F. DYUBKO, R. MOTIENKO, J. T. HOUGEN

B21 – *MILLIMETER WAVE SPECTRUM OF ACETAMIDE*
V. V. ILYUSHYN, E. A. ALEKSEEV, S. F. DYUBKO, I. KLEINER, J. T. HOUGEN

B22 – *MICROWAVE SPECTRUM AND CONFORMATIONAL ANALYSIS OF TWO CONFORMERS OF JET-COOLED ETHYL ACETAMIDOACETATE, A PEPTIDE MIMETIC*

R. J. LAVRICH, A. R. HIGHT WALKER, D. F. PLUSQUELLIC, G. T. FRASER, and J. T. HOUGEN, I. KLEINER

B23 – *MILLIMETER-WAVE SPECTROSCOPY OF NC_4P*
L. BIZZOCCHI and C. DEGLI ESPOSTI

B24 – *OPTIMAL STRATEGIES FOR REPRESENTING DIATOMIC MOLECULE DATA SETS*
ROBERT J. LE ROY

B25 – *STUDY OF THE MILLIMETER-WAVE SPECTRA OF THE LOWEST VIBRATIONAL STATES OF 1,1,1-DIFLUOROCHLOROETHANE*
OLEG BASKAKOV, V. ILYUSHIN, E. ALEKSEEV, E. ROBERTSON, D. McNAUGHTON

B26 – *THE HIGH RESOLUTION INFRARED SPECTRA OF ISOXAZOLE AND A COMPARISON WITH THEORETICAL STUDIES*
MICHAEL H. PALMER, FLEMMING HEGELUND, BENGT NELANDER and RENE WUGT LARSEN

B27 – *ANALYSIS OF HIGH RESOLUTION FTIR SPECTRA OF $CH_2{}^{79}Br^{35}Cl$. THE ν_4 AND ν_5 FUNDAMENTALS AND THEIR HOT-BANDS $\nu_4+\nu_6-\nu_6$ AND $\nu_5+\nu_6-\nu_6$*
MARCEL SNELS, GIUSEPPE D'AMICO

B28 – *DIODE LASER SLIT JET SPECTRA AND ANALYSIS OF THE ν_{14} FUNDAMENTAL OF 1,1,1,2-TETRAFLUOROETHANE (HFC-134a)*
MARCEL SNELS, GIUSEPPE D'AMICO

B29 – *INFRARED LASER SPECTRUM OF THE P=O (ν_2) FUNDAMENTAL BAND OF CIS–HOPO*
P.J. O'SULLIVAN, P.A. HAMILTON, P.B. DAVIES

B30 – *ANALYSIS OF $D_2^{16}O$ EMISSION SPECTRUM IN THE 320 - 860 cm^{-1} SPECTRAL RANGE*
GEORG CH. MELLAU, E.N. STARIKOVA, S.N. MIKHAILENKO, S.A. TASHKUN, VL.G. TYUTEREV

B31 – *HIGH-RESOLUTION ABSORPTION SPECTROSCOPY OF AN UNSTABLE SPECIES IN THE FAR-INFRARED: TENTATIVE ASSIGNMENT TO TRANS-PERP-HOONO*
J. ORPHAL, O. PIRALI, AND P.-M. FLAUD

B32 – *THE HIGHLY RESOLVED INFRARED SPECTRUM OF CDBrClF BETWEEN 600-1300 AND 1850-2300 cm^{-1}: DETECTION OF RESONANCES, OVERTONES AND COMBINATION BANDS*
SIEGHARD ALBERT AND MARTIN QUACK

B33 – *THE ν_{19a} BAND OF FLUOROBENZENE*
F. J. BASTERRETXEA, R. ESCRIBANO

B34 – *FIRST HIGH-RESOLUTION DETERMINATION OF THE ν_9 BAND CENTER of $^{35}ClONO_2$*
J.-M. FLAUD, J. ORPHAL, W. J. LAFFERTY, M. BIRK, AND G. WAGNER

B35 – *HIGH RESOLUTION RAMAN SPECTRA OF $^{12}C_2H_4$: THE ν_2 AND ν_3 FUNDAMENTALS AND THE $2\nu_{10}$ OVERTONE BAND*
DIONISIO BERMEJO, RAFAEL ESCRIBANO, JOSÉ LUIS DOMÉNECH, ROUL MARTÍNEZ, ELISABETTA CANÉ, LUCIANO FUSINA, GIANFRANCO DI LONARDO

B36 – *HIGH RESOLUTION INFRARED AND RAMAN SPECTRA OF $^{13}C_2D_2$: ANHARMONIC RESONANCE INTERACTIONS IN THE BENDING MANIFOLD ASSOCIATED WITH ν_3*
DIONISIO BERMEJO, JOSÉ LUIS DOMÉNECH, LUCIANO FUSINA, GIANFRANCO DI LONARDO

B37 – *HIGH-RESOLUTION INFRARED SPECTRA OF HCF_3 IN THE ν_6 AND $2\nu_6$ REGIONS: ROVIBRATIONAL ANALYSIS AND ACCURATE DETERMINATION OF THE GROUND STATE CONSTANTS C_0 AND D_K^0*
ADINA CEAUSU-VELCESCU, JEAN COSLÉOU, JEAN DEMAISON, HANS BÜRGER, GEORGES GRANER

B38 – *LINE INTENSITY MEASUREMENTS IN $^{14}N_2^{16}O$ AND THEIR TREATMENT USING THE EFFECTIVE OPERATOR APPROACH. II. THE 5200 TO 6400 cm^{-1} REGION*
L. DAUMONT,J-L. TEFFO, V. I. PEREVALOV, S. A. TASHKUN, J. VANDER AUWERA

B39 – *A NEW EXCITATION MECHANISM FOR INTERSTELLAR CLASS II METHANOL MASER TRANSITIONS BETWEEN FINE LEVELS*
HANPING LIU, JIN SUN

Invited Lectures C, Monday, September 8, 14:00

Chairman : L. FUSINA

C1 – *MASS-SELECTIVE INFRARED SPECTROSCOPY AND RELATED HIGH RESOLUTION SPECTROSCOPIC TECHNIQUES FOR INTRAMOLECULAR DYNAMICS (45 min.)*
MICHAEL HIPPLER

C2 – *OVERVIEW OF CAVITY-ENHANCED ABSORPTION MEASUREMENTS (45 min.)*
RICHARD N. ZARE

MOLECULAR PHYSICS Lecture.

Poster Session D, Monday, September 8, 16:00

D1 – *WEAK OVERTONE TRANSITIONS OF N_2O AROUND 1.05 μm BY ICLAS-VECSEL*
Y. DING, E. BERTSEVA AND A. CAMPARGUE, V. I. PEREVALOV, S. A. TASHKUN, J. -L. TEFFO, S. HU

D2 – *INCOHERENT BROAD-BAND CAVITY ENHANCED ABSORPTION SPECTROSCOPY*
ALBERT A. RUTH, SVEN E. FIEDLER, ACHIM HESE

D3 – *CAVITY RINGDOWN ABSORPTION SPECTRUM AND RING-BENDING POTENTIAL ENERGY FUNCTION OF THE $T_1(n,\pi^*)$ STATE OF 2-CYCLOPENTEN-1-ONE*
NATHAN R. PILLSBURY, STEPHEN DRUCKER, JAEBUM CHOO, JAAN LAANE

D4 – *A COMPARISON OF WAVELENGTH MODULATION AND CAVITY ENHANCED ABSORPTION SPECTROSCOPY FOR TRACE MOLECULE DETECTION IN THE NIR*
S. WALKER, G. DUXBURY and N. LANGFORD

D5 – *ROTATIONALLY RESOLVED OVERTONE COMBINATION BANDS OF FORMALDEHYDE AT 1.5 μm INVESTIGATED BY CAVITY ENHANCED ABSORPTION SPECTROSCOPY*
MICHAEL STAAK, EDWARD W. GASH, ALBERT A. RUTH

D6 – *CAVITY-ENHANCED BROAD-BAND ABSORPTION SPECTROSCOPY WITH A FEMTOSECOND LASER: APPLICATION TO THE OVERTONE SPECTROSCOPY OF ACETYLENE IN THE BLUE*
T. GHERMAN, S. KASSI, A. CAMPARGUE AND D. ROMANINI

D7 – *FIRST STUDY OF JET-COOLED BIS(BENZENE)CHROMIUM BY HIGH-RESOLUTION REMPI AND ZEKE-MATI SPECTROSCOPY*
SERGEY YU. KETKOV, HEINRICH L. SELZLE
and EDWARD W. SCHLAG

D8 – *TWO-COLOR REMPI SPECTROSCOPY OF JET-COOLED FERROCENE AND NICKELOCENE*
SERGEY YU. KETKOV, HEINRICH L. SELZLE
and EDWARD W. SCHLAG

D9 – *CALCULATING THE ENERGY LEVELS OF ISOMERIZING TETRAATOMIC MOLECULES: THE ROVIBRATIONAL STATES OF Ar_2HF*
IGOR N. KOZIN, MARK M. LAW, JEREMY M. HUTSON, JONATHAN TENNYSON

D10 – *ARE THE SPLITTINGS IN THE ν_6 FUNDAMENTAL OF 1-CHLORO-1,1-DIFLUOROETHANE (HCFC-142b) CAUSED BY INTERACTION WITH AN HIGHLY EXCITED TORSIONAL LEVEL?*
MARCEL SNELS, GIUSEPPE D'AMICO

D11 – *CALCULATION OF SPECTROSCOPIC CONSTANTS AND EFFECTIVE ROVIBRATIONAL PARAMETERS FOR TRIATOMIC C_{2v} AND C_s ISOTOPOMERS FROM POTENTIAL ENERGY FUNCTIONS*
H. SEGHIR , VL. G. TYUTEREV, S. A. TASHKUN

D12 – *COMPUTER IMPLEMENTATION OF CONTACT TRANSFORMATIONS FOR ROVIBRATIONAL HAMILTONIANS : MOL_CT CODE OF FORMAL CALCULATIONS*
S. A. TASHKUN, VL. G. TYUTEREV, H. SEGHIR

D13 – *CALCULATING THE ENERGY LEVELS OF ISOMERIZING TETRAATOMIC MOLECULES: THE WAVR4 CODE AND APPLICATION TO THE VIBRATIONAL STATES OF ACETYLENE/VINYLIDENE*
IGOR N. KOZIN, MARK M. LAW, JONATHAN TENNYSON, JEREMY M. HUTSON

D14 – *THE N=2 CH-CHROMOPHORE ABSORPTION NEAR 6000 CM^{-1} OF BENZENE ISOTOPOMERS BY MASS-SELECTIVE OVERTONE SPECTROSCOPY WITH IR+UV IONISATION DETECTION*
MICHAEL HIPPLER, ROBERT PFAB, MARTIN QUACK

D15 – *MULTIPHOTON ABSORPTION SPECTROSCOPY: REMPI-TOF ANALYSIS OF HCl AND DCl*
A. KVARAN and H. WANG

D16 – *RYDBERG-STATE-RESOLVED THRESHOLD-IONIZATION SPECTROSCOPY: APPLICATION TO CO^+ AND NH_3^+*
ROBERT SEILER, URS HOLLENSTEIN, and FREDERIC MERKT

D17 – *MOLECULAR ASSOCIATION IN METHANOL AND ETHANOL*
V.POGORELOV, L.SAVRANSKY, O.LIZENGEVICH, I.DOROSHENKO, E.FESJUN and O.VERETENNIKOV

D18 – *INTRAMOLECULAR HYDROGEN BOND DYNAMICS IN X-CH_2-CH_2-X, X=CH_3, NH_2, PH_2, OH, SH*
I. MERKE and W. STAHL

D19 – *NEGATIVE ION MOTION IN THE MIXTURES OF SF_6 WITH CF_4 AND CH_4-ARGON*
F. B. YOUSIF, J. DE URQUIJO

D20 – *MOLECULAR MATTER WAVE INTERFEROMETRY: TOOL FOR STUDYING WEAK INFLUENCES ON MOLECULES AND HIGH PRECISION MOLECULAR BEAM SPECTROSCOPY?*
IVAN SHERSTOV, MATTHIAS FRANK, HORST KNÖCKEL, EBERHARD TIEMANN

D21 – *INELASTIC SPUTTERING OF IONIC CRYSTALS UNDER ELECTRON AND MULTICHARGED ION BOMBARDMENT*
M.S. HUCHKAROV, B. RAHMONOVA, M.M. KUCHKAROVA, B.G. ATABAEV

D22 – *A METHOD OF CALCULATING ANHARMONIC VIBRATIONAL SPECTRA OF MOLECULES*
B. K. NOVOSADOV

D23 – *ABSOLUTE LINE INTENSITIES FOR CARBONYL SULFIDE NEAR* 4.85 *μm*
J. VANDER AUWERA, R. EL HACHTOUKI, K. AMARA, A. FAYT

D24 – *HIGH RESOLULTION SPECTROSCOPIC STUDIES OF VIBRATIONAL STATES IN THE TRIPLET POTENTIAL SURFACES OF ACETYLENE*
K. YOSHIDA, and H. KANAMORI

D25 – *CLASSICAL TRAJECTORY AND STATISTICAL PHYSICS PARTITIONING IN THE PHASE SPACE OF CO_2–Ar*
ANDREI A. VIGASIN, SERGEY E. LOKSHTANOV, SERGEY V. IVANOV

D26 – *THEORETICAL INVESTIGATION OF THE LOWEST-LYING STATES OF TRANSITION METAL MONOHALIDES LACl AND YI*
A. R. ALLOUCHE, S. ABDUL-AL, H. FAHS, M. AUBERT-FRECON, M. KOREK

D27 – *HIGH-RESOLUTION SPECTROSCOPY OF HOBr IN THE FAR- AND NEAR-INFRARED*
J. ORPHAL, Q. KOU, F. KWABIA TCHANA, O. PIRALI, AND J.-M. FLAUD

D28 – *FTS SPECTRA OF ISOTOPOMERS OF THE HYDROGEN SULFIDE IN THE INFRARED REGION*
L. REGALIA-JARLOT, Vl.G. TYUTEREV, J. MALICET, X. THOMAS, P. VON DER HEYDEN, Yu. BORKOV

D29 – *HIGH RESOLUTION FTIR SPECTROSCOPY ON CH_2DI AND CHD_2I: EVALUATION OF THE GROUND STATE CONSTANTS AND ANALYSIS OF THE ν_3 BANDS*
S. ALANKO, K. KYLLÖNEN, J. LOHILAHTI and V.– M. HORNEMAN

D30 – *THE C–H BENDING VIBRATION ν_4 OF CHLOROFORM $CH^{35}Cl_3$*
S. ALANKO, V.-M. HORNEMAN, and R. ANTTILA

D31 – *THE ν_1 AND ν_3 INFRARED BANDS OF $^{12}C_2HD$ AND $^{13}C_2HD$ OBSERVED BY FOURIER TRANSFORM SPECTROSCOPY*
GIANFRANCO DI LONARDO, LUCIANO FUSINA, FILIPPO TAMASSIA

D32 – *ANALYSIS OF THE $\nu_7 + \nu_9$ BAND OF DICYANOACETYLENE (NC-CC-CN)*
FLEMMING WINTHER, VELI-MATTI HORNEMAN, CORINNE VIGOUROUX and ANDRE FAYT

D33 – *HIGH RESOLUTION SPECTRUM OF CH_3D IN THE REGIONS OF 3950 - 4600 AND 5700 - 6150 CM^{-1}: ROTATIONAL ASSIGNMENT AND PRELIMINARY ANALYSIS*
O. N. ULENIKOV, E. S. BEKHTEREVA, H. HOLLENSTEIN, M. QUACK

D34 – *ANALYSIS OF THE FIRST HIGH RESOLUTION FT INFRARED SPECTRA OF $F_2{}^{11}BOH$: THE ν_5, ν_8, ν_9, $2\nu_9$ $\nu_8+\nu_9$, AND ν_4 BANDS*
A. PERRIN, J.-M. FLAUD, M.CARVAJAL-ZAERA, J.DEMAISON, J.F.D'EU, H. BÜRGER, D.COLLET

D35 – *FIRST HIGH-RESOLUTION FTIR ANALYSIS OF THE ν_9 BAND OF CH_2DF AND CONNECTION WITH THE NEAR ν_5 AND ν_6 VIBRATIONAL LEVELS*
A. BALDACCI, R. VISINONI, G. NIVELLINI

D36 – *HIGH-RESOLUTION ABSORPTION SPECTRA OF ISOTOPIC SPECIES OF CARBON DIOXIDE CONTAINING ^{13}C*
Y. DING, L.Y. HAO, S.M. HU, V.I. PEREVALOV, S.A. TASHKUN, J.-L. TEFFO

D37 – *ROVIBRATIONAL ANALYSIS OF THE ν_4 AND THE $\nu_5+\nu_9$ BANDS OF $CH^{35}Cl_2F$*
SIEGHARD ALBERT AND MARTIN QUACK

D38 – *HIGH-RESOLUTION FAR-INFRARED FOURIER-TRANSFORM ABSORPTION SPECTROSCOPY OF THE CIS- AND TRANS-ISOMERS OF NITROUS ACID (HONO) AND ITS DEUTERATED ISOTOPOMERS (CIS- AND TRANS-DONO)*
O. PIRALI, J. ORPHAL, P.-M. FLAUD, and M. VERVLOET

D39 – *NEW ANALYSIS OF THE ν_2, ν_3, ν_4 AND ν_6 BANDS OF FORMALDEHYDE $H_2{}^{12}C^{16}O$. LINE POSITIONS AND INTENSITIES IN THE 5-10 μm SPECTRAL REGION*
F. KELLER, A. PERRIN, AND J.-M. FLAUD

Invited Lectures E, Tuesday, September 9, 9:00

Chairman : R. ZARE

E1 – *FOURIER TRANSFORM INTRACAVITY LASER ABSORPTION SPECTROSCOPY (20 min.)*
DANIEL HURTMANS

E2 – *CAVITY ENHANCED ABSORPTION SPECTROSCOPY, FROM DIODE LASERS TO MODELOCKED LASERS (20 min.)*
D. ROMANINI, J. MORVILLE, T. GHERMAN, S. KASSI, N. SADEGHI, A. CAMPARGUE, and M. CHENEVIER

E3 – *$Ar\cdots I_2$: A MODEL SYSTEM FOR COMPLEX DYNAMICS (45 min.)*
A. BUCHACHENKO, N. HALBERSTADT, B. LEPETIT, and O. RONCERO

Poster Session F, Tuesday, September 9, 11:00

F1 – *DECAGONAL QUASIPERIODIC STRUCTURES VIA ATOM-OPTICAL NANOFABRICATION*
G. MYSZKIEWICZ, E. JURDIK, J. HOHLFELD, W.L. MEERTS, H. VAN KEMPEN AND TH. RASING
AMAT MILLS Award Applicant.

F2 – *FREE JET ROTATIONAL SPECTRA AND HYDROGEN BONDING: OXETANE-WATER*
B. MICHELA GIULIANO, PAOLO OTTAVIANI, BIAGIO VELINO and WALTHER CAMINATI
AMAT MILLS Award Applicant.

F3 – *SPECTROSCOPY OF OCTAHEDRAL MOLECULES IN A DEGENERATE ELECTRONIC STATE: DETAILED INVESTIGATION OF THE 720 cm^{-1} REGION OF JET-COOLED ReF_6*
M. REY, V. BOUDON, M. ROTGER and M. LOETE, H. HOLLENSTEIN and M. QUACK
AMAT MILLS Award Applicant.

F4 – *SURPRISINGLY LARGE PARITY VIOLATING ENERGY DIFFERENCES IN ENANTIOMERS WHICH ARE CHIRAL BY ISOTOPIC SUBSTITUTION: THEORY AND INITIAL SPECTROSCOPIC STUDIES*
A. SIEBEN, R. BERGER, M. QUACK, AND M. WILLEKE
AMAT MILLS Award Applicant.

F5 – *THE ROTATIONAL SPECTRUM OF THE He-HCCCN VAN DER WAALS COMPLEX: A COMPARISON OF EXPERIMENT AND THEORY*
WENDY C. TOPIC, AIKO HUCKAUF, and WOLFGANG JÄGER
AMAT MILLS Award Applicant.

F6 – *THE DOUBLE RENNER EFFECT IN A TRIATOMIC MOLECULE*
TINA E. ODAKA, PER JENSEN, and TSUNEO HIRANO
AMAT MILLS Award Applicant.

F7 – *ICLAS-VECSEL: I SPECTRAL CONDENSATION*
ELENA BERTSEVA, ALAIN CAMPARGUE
AMAT MILLS Award Applicant.

F8 – *TIME-RESOLVED FOURIER TRANSFORM INTRACAVITY LASER ABSORPTION SPECTROSCOPY AROUND 1 μm*
F. GUEYE, G. GUELACHVILI, N. PICQUÉ, V. DANA, J.-Y. MANDIN

F9 – *OPTICAL ABSORPTION SPECTROSCOPY OF THE CIRCUMSTELLAR ENVELOPE OF IRC +10216 USING BACKGROUND STARS*
T. R. KENDALL, N. MAURON, J. McCOMBIE and P. J. SARRE

F10 – *THE UIR EMISSION FEATURES OF THE RED RECTANGLE*
I.-O. SONG, J. McCOMBIE, P. A. COUCH, P. J. SARRE, T. H. KERR

F11 – *HIGH-RESOLUTION FOURIER-TRANSFORM INTRA-CAVITY LASER ABSORPTION SPECTROSCOPY: APPLICATION TO $^{12}C_2H_2$ NEAR 12300 cm^{-1}*
S.M. HU, A. CAMPARGUE, Y. DING, Z.Y. WU, A.W. LIU

F12 – *ICLAS-VECSEL: II HIGH SENSITIVITY OVERTONE SPECTROSCOPY OF HDO, H_2O AND ACETYLENE NEAR 1.05 μm*
A. CAMPARGUE, E. BERTSEVA, O. NAUMENKO, Y. DING, S. HU

F13 – *BAND SHAPES IN THE INFRARED SPECTRA OF VAN DER WAALS-BONDED NANOPARTICLES*
R. GEORGES, E. HUGO, and A. BENIDAR

F14 – *HIGH SENSITIVITY CW-CRDS OF H_2O IN ATMOSPHERIC SPECTRAL WINDOWS*
P. MACKO, S. KASSI, D. ROMANINI, A. CAMPARGUE, K. PFEILSTICKER

F15 – *FOURIER TRANSFORM – INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF C_2HD*
D. HURTMANS, C. DEPIESSE, J. VANDER AUWERA, and M. HERMAN, S. KASSI, G. DI LONARDO, L. FUSINA, A. FAYT

F16 – *FREQUENCY MODULATION TRANSIENT LASER ABSORPTION SPECTROSCOPY OF TiS $E^3\Pi$ - $X^3\Delta$*
KAORI KOBAYASHI, and HIDETO KANAMORI

F17 – *CONCENTRATION MEASUREMENTS OF OZONE IN THE 1200 TO 300 PPBV RANGE: AN INTERCOMPARAISON BETWEEN THE B. N. M. ULTRAVIOLET STANDARD AND INFRARED METHODS*
G. DUFOUR, A. HENRY, C. CAMY-PEYRET and A. VALENTIN, D. HURTMANS

F18 – *DEVELOPMENT OF A STABILIZED LOW TEMPERATURE INFRARED ABSORPTION CELL FOR USE IN STANDARD LOW TEMPERATURE AND COLLISIONAL COOLING EXPERIMENTS*
A. VALENTIN, A. HENRY, C. CLAVEAU, D. HURTMANS, A. W. MANTZ

F19 – *ROTATIONAL AND VIBRATIONAL ANALYSES OF THE MgNC $\tilde{A}\ ^2\Pi$ - $\tilde{X}\ ^2\Sigma^+$ TRANSITION*
MASARU FUKUSHIMA and TAKASHI ISHIWATA

F20 – *DEPERTURBATION ANALYSIS OF THE $A^2\Pi \sim B^2\Sigma^+$ INTERACTION OF SrBr*
CAMERON S. DICKINSON, and JOHN A. COXON

F21 – *THE [0.25]$X^2\Pi_{1/2}$ SPIN-ORBIT COMPONENT OF NiF*
M. BENOMIER, B. PINCHEMEL, P. F. BERNATH, M. TANIMOTO, T. OKABAYASHI

F22 – *THE VISIBLE SPECTRUM OF CoCl BETWEEN 19,000 AND 23,000 CM^{-1}*
T. HIRAO, B. PINCHEMEL, P. F. BERNATH

F23 – *PARTITION SUMS AND DISSOCIATION ENERGY FOR $^{12}C^{16}O_2$ AT HIGH TEMPERATURES*
VLADIMIR OSIPOV

F24 – *MULTIDIMENSIONAL VIBRATIONAL MODEL FOR 5- METHYLTROPOLONE*
M. KREGLEWSKI

F25 – *GEOMETRY OF $CaOCH_3$ FROM SPECTRA OF THE A $^2E \leftarrow$ X $^2A_1$ SYSTEM*
P. CROZET, A. J. ROSS, C. LINTON, M. J. DICK, A. G. ADAM and W. S. HOPKINS

F26 – *GLOBAL FITTING OF VIBRATION-ROTATION LINE POSITIONS OF ACETYLENE MOLECULE IN THE FAR AND MIDDLE INFRARED REGIONS*
O. M. LYULIN, V. I. PEREVALOV, J.-L. TEFFO

F27 – *DETERMINATION OF THE POTENTIAL SURFACE OF H_2O IN THE FRAMEWORK OF THE EXTENDED SU(2) MODEL*
RENATO LEMUS

F28 – *SU(4) IN ELECTRONIC SPECTROSCOPY OF MOLECULES WITH AN ODD NUMBER OF ELECTRONS*
FRANCOISE MICHELOT, MICHAËL REY, VINCENT BOUDON

F29 – *THE SPECTRUM OF SINGLET SiH_2*
SERGEI. N. YURCHENKO, P.R. BUNKER, W.P. KRAEMER, PER JENSEN

F30 – *ROVIBRONIC ENERGY LEVEL STRUCTURE OF THE ETHYLENE RADICAL CATION*
STEFAN WILLITSCH and FREDERIC MERKT

F31 – *HIGH-RESOLUTION FTIR AND MMW STUDY OF THE $V_4 = 2$ (A_1, E) EXCITED STATE OF $^{14}NF_3$ NEAR 985 CM^{-1}. THE AXIAL GROUND STATE CONSTANTS DERIVED BY THE LOOP METHOD*
N. BEN SARI-ZIZI, H. NAJIB, J. DEMAISON, B. BAKRI, J.-M. COLMONT, H. BÜRGER

F32 – *MILLIMETERWAVE SPECTRUM OF ETHYLENE*
JEAN DEMAISON, LAURENT MARGULES, BILAL BAKRI, and FRANCOIS HERLEMONT, ANDRE FAYT

F33 – *MICROWAVE MEASUREMENTS AND UPDATE OF OZONE GROUND STATE PARAMETERS*
J.-M. COLMONT, B. BAKRI, J. DEMAISON, H. MÄDER, F. WILLAERT, V.G. TYUTEREV, A. BARBE

F34 – *MICROWAVE SPECTRUM AND CONFORMATIONAL COMPOSITION OF ALLENYLPHOSPHINE, $H_2C{=}C{=}CHPH_2$*
HARALD MØLLENDAL, JEAN-CLAUDE GUILLEMIN, JEAN DEMAISON

F35 – *THE GROUND STATE ROTATIONAL SPECTRUM OF SO_2F_2*
M. ROTGER, V. BOUDON and M. LOËTE, L. MARGULÈS and J. DEMAISON, H. MÄDER, G. WINNEWISSER and H. S. P. MÜLLER

F36 – *ROTATIONAL SPECTRUM, HYPERFINE STRUCTURE, AND GEOMETRICAL STRUCTURE OF 2-AZETIDINONE*
K. DEMYK, D. PETITPREZ, G. WLODARCZAK, J. DEMAISON, H. MØLLENDAL

F37 – *THE TORSIONAL SPECTRUM OF THE PARTIALLY DEUTERATED SPECIES OF METHANOL CALCULATED FROM A MULTIDIMENSIONAL AB INITIO POTENTIAL*
S. BLASCO, D. LAUVERGNAT, AND L. H. COUDERT

F38 – *ANALYSIS OF THE HIGH RESOLUTION INFRARED SPECTRUM OF MONODEUTERATED ETHYLENE OXIDE BETWEEN 850-950 cm^{-1}*
KAREN KEPPLER ALBERT, SIEGHARD ALBERT AND MARTIN QUACK, JÜRGEN STOHNER, OLIVER TRAPP, VOLKER SCHURIG

F39 – *ANALYSIS OF SOME COMBINATION AND OVERTONE INFRARED ABSORPTION BANDS OF $^{32}S^{16}O_3$*
ALFONS WEBER, ARTHUR MAKI, T. A. BLAKE, S. W. SHARPE, AND R. L. SAMS, J. FRIEH, J. BARBER, T. MASIELLO, AND J. W. NIBLER

Invited Lectures G, Tuesday, September 9, 14:00

Chairman : L. S. ROTHMAN

G1 – *NEW CHALLENGES IN ATMOSPHERIC SPECTROSCOPY AFTER THE MIPAS EXPERIMENT (45 min.)*
BRUNO CARLI

G2 – *MOLECULES IN ASTROPHYSICS: THE NEED FOR HIGH-RESOLUTION SPECTROSCOPY (45 min.)*
EWINE F. VAN DISHOECK

Poster Session H, Tuesday, September 9, 16:00

H1 – *REAL TIME DETECTION OF ETHYLENE IN AUTOMOBILE EXHAUSTS AND CIGARETTE SMOKE*
M. T. MCCULLOCH, E. L. NORMAND, G. DUXBURY and N. LANGFORD
AMAT MILLS Award Applicant.

H2 – *GLOBAL ANALYSIS OF NEW FT EMISSION SPECTRA OF THE C_2 SWAN SYSTEM*
A. TANABASHI, T. HIRAO and T. AMANO, P. F. BERNATH
AMAT MILLS Award Applicant.

H3 – *STUDY OF THE LOW-ENERGY STRUCTURE OF SOME ASTROPHYSICAL SPECIES BY FOURIER-TRANSFORM SPECTROSCOPY*
O. PIRALI, M. VERVLOET

AMAT MILLS Award Applicant.

H4 – *STUDY OF THE ROTATIONAL SPECTRA OF $(CH_3)_3SnCl$ and $(CH_3)_2SiH$-$Sn(CH_3)_3$*
MELANIE SCHNELL, DEIKE BANSER, JENS-UWE GRABOW

AMAT MILLS Award Applicant.

H5 – *EXTREME ULTRAVIOLET LASER EXCITATION OF ISOTOPIC MOLECULAR NITROGEN*
J.P. SPRENGERS, W. UBACHS, K.G.H. BALDWIN, B.R. LEWIS, W.-Ü L. TCHANG-BRILLET, A. JOHANSSON, A. L'HUILLIER, C.-G. WAHLSTRÖM

AMAT MILLS Award Applicant.

H6 – *THE ROTATIONAL SPECTRUM OF CHLOROMETHANOL, A POSSIBLE CHLORINE RESERVOIR SPECIES*
DEIKE BANSER, MELANIE SCHNELL, JENS-UWE GRABOW

AMAT MILLS Award Applicant.

H7 – *MODIFIED DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY SYSTEM USING NEURAL NETWORKS AND COMPUTER SIMULATION*
A. MOHAMMADI, H. NADGARAN, H. CHIZARI

AMAT MILLS Award Applicant.

H8 – *THE DETECTION OF THE ELECTRONIC SPECTRUM OF $FeCl_2$ IN THE GAS PHASE*
STEPHEN H. ASHWORTH, PHILIP J. HODGES and JOHN M. BROWN

AMAT MILLS Award Applicant.

H9 – *NEW SPECTROSCOPIC DATA OF CHLOROFLUOROCARBONS AND HYDROCHLOROFLUOROCARBONS IN SUPPORT OF THE ANALYSIS OF ATMOSPHERIC DATA, OBTAINED BY HIGH RESOLUTION INFRARED SPECTROSCOPY*
MARCEL SNELS, PAOLA MASSOLI, GIUSEPPE D'AMICO

H10 – *THEORETICAL CALCULATION OF CONTINUUM ATMOSPHERIC ABSORPTION IN THE MILLIMETER AND FAR-INFRARED REGIONS*
R. H. TIPPING, Q. MA

H11 – *LINE STRENGTHS AND HALF-WIDTHS OF N_2O AND CO_2 BANDS IN THE 2100–3800 CM^{-1} REGION AT ATMOSPHERIC TEMPERATURES*
M.FUKABORI, T.AOKI, T.WATANABE

H12 – *FAR INFRARED COMPENSATION EFFECT IN THE ATMOSPHERE*
FERENC M. MISKOLCZI, MARTIN G. MLYNCZAK

H13 – *MILLENIUM HITRAN COMPILATION*
L.S. ROTHMAN, D. JACQUEMART, and K. CHANCE

H14 – *THE NEXT HITRAN EDITION: DESCRIPTION OF NEW PARAMETERS*
D. JACQUEMART and L.S. ROTHMAN

H15 – *THE COLOGNE DATABASE FOR MOLECULAR SPECTROSCOPY, CDMS*
HOLGER S. P. MÜLLER, SVEN THORWIRTH, and GISBERT WINNEWISSER

H16 – *NEW FEATURES OF THE MOGADOC DATABASE (MOLECULAR GAS-PHASE DOCUMENTATION)*
JÜRGEN VOGT and NATALJA VOGT

H17 – *STARK SPECTROSCOPY OF THE ETHYLENE MOLECULE : TENSORIAL FORMALISM FOR SPECTRUM SIMULATIONS*
W. RABALLAND, M. ROTGER, V. BOUDON, M. LOËTE

H18 – *D_{2h} TOP DATA SYSTEM (D_{2h}TDS) SOFTWARE FOR SPECTRUM SIMULATION OF X_2Y_4 ASYMMETRIC MOLECULES*
W. RABALLAND, CH. WENGER, M. ROTGER, V. BOUDON, M. LOËTE

H19 – *CDSD-1000, THE HIGH-TEMPERATURE CARBON DIOXIDE SPECTROSCOPIC DATABANK AND INFORMATION SYSTEM*
S. A. TASHKUN, V. I. PEREVALOV, Y. L. BABIKOV, J.-L. TEFFO, A. D. BYKOV and N. N. LAVRENTIEVA

H20 – *SELF-BROADENING COEFFICIENTS IN THE ν_4 BAND OF CH_4 BY DIODE-LASER SPECTROSCOPY*
M. LEPÈRE*, M. LENGELÉ, J. WALRAND, G. BLANQUET

H21 – *TEST OF THEORETICAL LINESHAPES FITTED TO EXPERIMENTAL PROFILES FOR CH_3D LINES BROADENED BY Xe*
Ch. LEROT, G. BLANQUET, J. WALRAND, M. LEPÈRE*, J.-P. BOUANICH

H22 – *DIODE-LASER MEASUREMENTS OF SELF-BROADENING COEFFICIENTS IN ETHYLENE AT ROOM AND LOW TEMPERATURES*
G. BLANQUET, M. LEPÈRE*, J. WALRAND, J.-P. BOUANICH

H23 – *ABSORPTION OSCILLATOR STRENGTHS OF $^{12}C^{16}O$ and $^{13}C^{16}O$ IN THE VUV*
M. EIDELSBERG, J.L. LEMAIRE, J.H. FILLION, F. ROSTAS, S. FEDERMAN, Y. SHEFFER

H24 – *NEW ANALYSIS OF THE ν_5 AND $2\nu_9$ BANDS OF HNO_3: LINE POSITIONS AND LINE INTENSITIES*
A. PERRIN, J. ORPHAL, J.-M. FLAUD, S. KLEE, G. C. MELLAU, H. MÄDER, D. WALBRODT, M. WINNEWISSER

H25 – *ON COLLISION-INDUCED ABSORPTION IN PURE O_2, CO_2 AND CO_2 – O_2 MIXTURES*
Y. I. BARANOV, W. J. LAFFERTY AND G. T. FRASER

H26 – *AN EXAMINATION OF THE ENERGY CORRECTED SUDDEN SCALING PROCEDURE FOR THE CALCULATION OF ROTATIONAL RELAXATION OF CO IN ARGON*
R. Z. MARTINEZ, J. L. DOMENECH, D. BERMEJO, F. THIBAULT, J. P. BOUANICH, C. BOULET

H27 – *SIMULATION OF THE SHPOLSKII SPECTRUM IN THE FRAMEWORK OF THE SIMPLEST π-ELECTRONIC MODEL*
M. M. MESTECHKIN, and A. L. WUL'FOV

H28 – *INTERACTIONS IN SYMMETRIC TOP MOLECULES BETWEEN VIBRATIONAL POLYADS: ROTATIONAL AND ROVIBRATIONAL SPECTROSCOPY OF LOW-LYING STATES OF PROPYNE, H_3C–$C{\equiv}CH$*
HOLGER S. P. MÜLLER, PETR PRACNA, VELI-MATTI HORNEMAN, STEFAN KLEE

H29 – *METHOD OF CORRECTED GREEN FUNCTION FOR CALCULATING FREQUENCY-DEPENDENT CHARACTERISTICS OF ATOMS AND MOLECULES*
BORIS A. ZON, DMITRY DOROFEEV, IGOR KRETININ

H30 – *HIGHLY EXCITED $(6)^1\Sigma_u^+$ AND $(7)^1\Pi_u$ STATES OF K_2 FROM POLARIZATION LABELLING SPECTROSCOPY AND AB INITIO CALCULATIONS*
A. GROCHOLA, W. JASNIECKI, P. KOWALCZYK, W. JASTRZEBSKI, A. R. ALLOUCHE, M. AUBERT-FRECON, S. MAGNIER

H31 – *THEORETICAL SPIN-ORBIT STRUCTURE FOR THE ALKALI DIMER CATIONS K_2^+, Rb_2^+ AND Cs_2^+*
M. AUBERT-FRECON, A. JRAIJ, S. MAGNIER, M. KOREK

H32 – *POSITIONS AND INTENSITIES OF ^{18}O OZONE ENRICHED ISOTOPOMERS : THE 5 μm REGION REVISITED*
M.-R. DE BACKER-BARILLY, A. BARBE, Vl.G. TUYTEREV, S.A. TASHKUN

H33 – *NEW ANALYSIS OF THE CORIOLIS-INTERACTING ν_2 AND ν_5 BANDS OF CH_3Br : LINE POSITIONS AND INTENSITIES*
F. KWABIA TCHANA, I. KLEINER, J. ORPHAL, N. LACOME, O. BOUBA

H34 – *DYNAMICAL STRUCTURE OF PEPTIDE MOLECULES USING FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATION: N-METHYLFORMAMIDE, N-ETHYLACETAMIDE*
YOSHIYUKI KAWASHIMA, TSUYOSHI USAMI, KEISUKE OHBA, RICHARD D. SUENRAM, YU GOLUBIATNIKOV, EIZI HIROTA

H35 – *ROVIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF THE* $v_2 = 1$, $v_5 = 1$, *AND* $v_3 = 2$ *LEVELS OF* $^{13}CH_3{}^{37}Cl$
P. PRACNA, F.L. CONSTANTIN, J. DEMAISON, H. BÜRGER, L. FÉJARD

H36 – *THE PURE ROTATION SPECTRUM AND THE VIBRATIONAL FUNDAMENTALS OF* $^{123}SbD_3$
E. CANÉ, L. FUSINA, H. BÜRGER, W. JERZEMBECK

H37 – *HIGH RESOLUTION RO-VIBRATIONAL ANALYSIS OF VIBRATIONAL STATES OF* A_2 *SYMMETRY OF THE DIDEUTERATED METHANE* CH_2D_2
O. N. ULENIKOV, E. S. BEKHTEREVA, H. HOLLENSTEIN, M. QUACK

H38 – *HIGH RESOLUTION SPECTRUM OF* CH_2D_2*: THE* $2\nu_9$, $\nu_3 + \nu_4$, $\nu_5 + \nu_9$, $\nu_5 + \nu_7$, *AND* $\nu_3 + \nu_7$ *BANDS*
O. N. ULENIKOV, E. S. BEKHTEREVA, H. HOLLENSTEIN, M. QUACK

H39 – *CALCULATION OF NEW LINELISTS FOR WATER ISOTOPOMERS AND ANALYSIS OF EXPERIMENTAL SPECTRA*
MIZUHO TANAKA, JONATHAN TENNYSON, JAMES W. BRAULT, WIM UBACHS, MAARTEN SNEEP

Invited Lectures I, Wednesday, September 10, 9:00

Chairman : T. R. HUET

I1 – *LASER SPECTROSCOPY OF ISOLATED DNA BASES AND BASE PAIRS: STRUCTURE AND PHOTOCHEMISTRY (45 min.)*
K.KLEINERMANNS, CHR. PLÜTZER, I. HÜNIG

I2 – *STRUCTURES AND DYNAMICAL BEHAVIORS OF LARGE MOLECULES OF BIOLOGICAL SIGNIFICANCE IN A SOLVENT-FREE ENVIRONMENT (45 min.)*
W. LEO MEERTS

Poster Session J, Wednesday, September 10, 11:00

J1 – *PHOTOPHYSICS AND CONFORMATIONAL STRUCTURES OF BIOMOLECULES: ROTATIONAL BAND CONTOURS OF DNA BASE ADENINE AND AMINO ACID PHENYLALANINE*
YONGHOON LEE, JIWON JUNG, and BONGSOO KIM

J2 – *HIGH-RESOLUTION INFRARED ABSORPTION SPECTRUM AND ANALYSIS OF THE* $\nu_2 + \nu_4$ *COMBINATION BAND OF* SF_6
V. BOUDON, N. LACOME

J3 – *APPLICATION OF THE GENETIC ALGORITHM IN THE ANALYIS OF COMPLEX MOLECULAR SPECTRA*
W. LEO MEERTS, MICHAEL SCHMITT, GERRIT. C. GROENENBOOM

J4 – *APPLICATION OF PATTERN RECOGNITION METHOD TO PEAK SEARCHING AND LINE ASSIGNMENT*
L.N. SINITSA, O.V. NAUMENKO, A.M. PSHENICHNIKOV, A.P. SHCERBAKOV

J5 – *HIGH-RESOLUTION SPECTROSCOPY OF FLUOROSTYRENE, 3-METHYLINDOLE AND THEIR NOBLE GAS AND WATER CLUSTERS*
S. CHERVENKOV, P. WANG, T. CHAKRABORTY, and H. J. NEUSSER

J6 – *RECENT DEVELOPMENTS IN THE LASER SPECTROSCOPY OF LANTHANIDE HALIDES*
C. LINTON, M. J. DICK AND R. K. GHOSH

J7 – *LABORATORY SPECTROSCOPY OF SMALL CARBON CLUSTERS*
P. NEUBAUER-GUENTHER, T. F. GIESEN, U. BERNDT, G. FUCHS, and G. WINNEWISSER

J8 – *STUDYING CLUSTERS OF ORGANIC MOLECULES WITH Ar AND H_2O USING MASS ANALYZED THRESHOLD IONIZATION*
S. GEORGIEV, T. CHAKRABORTY, J. BRAUN, and H. J. NEUSSER

J9 – *ON THE USE OF CLASSICAL TRAJECTORIES IN LINEWIDTHS CALCULATIONS*
M. AFZELIUS, , J. BULDYREVA,P. JOUBERT, L. BONAMY and J. BONAMY

J10 – *COLLISIONAL BROADENING OF C_2H_2 ABSORPTION LINES BY AN EXACT TRAJECTORY APPROACH*
J. BULDYREVA

J11 – *PRECISE LINE STRENGTHS AND COLLISION BROADENING PARAMETERS FOR THE ν_3 BAND OF SO_2 DETERMINED BY DIFFERENCE FREQUENCY SPECTROSCOPY*
JES HENNINGSEN

J12 – *THE $X^2A_1 - A^2B_2$ CONICAL INTERSECTION IN NO_2: INTERPRETATION OF ICLAS, LIF AND LIDFS SPECTRA WITH A MODEL HAMILTONIAN*
R. JOST, M. JOYEUX AND A. CAMPARGUE

J13 – *MULTI-DIMENSIONAL ANHARMONIC RESONANCES AND PARITY VIOLATION IN CDBrClF*
JÜRGEN STOHNER, MARTIN QUACK

J14 – *TEST OF ABSORPTION LINE SHAPE MODELS: AN ILLUSTRATION FROM MILLIMETER, SUB-MILLIMETER AND INFRARED SPECTRA OF HCN*
F. ROHART, J.-M. COLMONT and G. WLODARCZAK

J15 – *LINE MIXING EFFECTS IN THE CF_4 VIBRATION-ROTATION SPECTRA*
A. V. DOMANSKAYA, N. N. FILIPPOV, and M. V. TONKOV

J16 – *STRUCTURE AND BAND SHAPE EVOLUTION OF THE ν_2 FORBIDDEN BAND OF CF_4*
M. V. TONKOV, A. V. PODZOROV, A. V. DOMANSKAYA, J. BOISSOLES

J17 – *INTERCOMPARISON BETWEEN OZONE BROADENING PARAMETERS RETRIEVED FROM MILLIMETRE-WAVE MEASUREMENTS BY USING DIFFERENT TECHNIQUE*
B. BAKRI, J.-M. COLMONT, J. DEMAISON, F. ROHART, G. WLODARCZAK, G. CAZZOLI, L. DORE, C. PUZZARINI, S. BENINATI

J18 – *HYPERFINE STRUCTURE OF S_2Cl_2*
A. MIZOGUCHI, S. OTA, and H. KANAMORI

J19 – *THE POTENTIAL ENERGY FUNCTION FOR THE ELECTRONIC GROUND STATE OF H_2Se DERIVED WITH THE MORBID APPROACH*
O. N. ULENIKOV, E. S. BEKHTEREVA, N. A. SANZHAROV, PER JENSEN

J20 – *ALGEBRAIC HAMILTONIAN ADAPTED TO STRECH - BEND COUPLING IN THE STIBINE MOLECULE*
LAURENT PLUCHART, CLAUDE LEROY, FRANCOISE MICHELOT, OLEG ULENIKOV

J21 – *VIBRATIONAL ENERGY LEVELS OF AMMONIA-TYPE MOLECULES WITH LARGE AMPLITUDE INVERSION MOTION*
TIMO RAJAMÄKI, ANDREA MIANI, LAURI HALONEN

J22 – *STEREOMUTATION DYNAMICS AND PARITY VIOLATION IN C_2 AND C_1 SYMMETRIC XYYX′ (XYZX′) TYPE MOLECULES*
MARTIN QUACK AND MARTIN WILLEKE

J23 – *INTERNAL ROTATION OF THE NO_2 GROUP IN LOWER NITROALKANES: NITROETHANE*
Yu. I. TARASOV, I. V. KOCHIKOV, A. V. STEPANOVA, B. K. NOVOSADOV, R. Z. DEYANOV, A. V. KLOCHENOK, N. VOGT and J. VOGT

J24 – *INTERNAL ROTATION ANALYSIS OF THE FT-MW SPECTRUM OF EIGHT ISOTOPOMERS OF DIMETHYL DISELENIDE*
PETER GRONER, CHARLES W. GILLIES, JENNIFER Z. GILLIES

J25 – *METHYL INTERNAL ROTATION IN SUBSTITUTED TOLUENES*
W. STAHL, I. MERKE, and A. HELLWEG

J26 – *MILLIMETER-WAVE SPECTRA OF THE $^{12}C^{16}O$ AND $^{13}C^{16}O$ DIMERS: ASSIGNMENT AND PRECISE LOCATION OF ENERGY LEVELS*
L. SURIN, D. FOURZIKOV, G. WINNEWISSER, B. DUMESH, J. TANG, A.R.W. McKELLAR

J27 – *MICROWAVE SPECTROSCOPY OF OPEN-SHELL VAN DER WAALS COMPLEXES*
B.J. WATSON, M.S. SNOW and B.J. HOWARD

J28 – *MICROWAVE SPECTROSCOPY OF THE WEAKLY BOUND COMPLEXES OF CHIRAL MOLECULES*
A. KING, J.P.I. HEARN and B.J. HOWARD

J29 – *A MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE STUDY OF 2-METHYLPYRIDINE AND ITS COMPLEX WITH AR: STRUCTURE, ^{14}N NUCLEAR QUADRUPOLE COUPLING AND METHYL INTERNAL ROTATION*
S. WÖRMKE, K. BRENDEL, H. MÄDER

J30 – *VIBRATIONAL ANALYSIS OF MEDIUM STRENGTH HYDROGEN BONDED HETERODIMERS : FTIR SPECTRA AND BAND CONTOUR ANALYSIS OF THE STRETCHING MODE OF H(D)F COMPLEXED WITH ORGANIC BASES*
P. ASSELIN,M. GOUBET, P. SOULARD, M. LEWERENZ

J31 – *THE MICROWAVE SPECTRA OF THE COMPLEXES OF FLUORINATED BENZENES WITH WATER*
K. BRENDEL, H. MÄDER

J32 – *ROTATIONAL SPECTRA OF He_N-N_2O (N=3-12) QUANTUM CLUSTERS*
YUNJIE XU and WOLFGANG JÄGER

J33 – *MILLIMETER-WAVE SPECTROSCOPY AND COUPLED CLUSTER CALCULATIONS FOR A NEW PHOSPHORUS-CARBON CHAIN: HC_5P*
L. BIZZOCCHI, C. DEGLI ESPOSTI, P. BOTSCHWINA

J34 – *DIODE LASER SPECTROSCOPY OF CO_2 IN THE 1.6 μm AND 2.0 μm REGIONS FOR ATMOSPHERIC APPLICATIONS*
V. ZENINARI, B. PARVITTE, L. JOLY, D. COURTOIS, I. POUCHET, G. DURRY, A. VICET

J35 – *SPECTROSCOPIC STUDY OF THE $(30^01) \leftarrow (000)$ BAND OF CO_2 WITH A DIODE LASER SPECTROMETER*
B. PARVITTE, V. ZENINARI, I. POUCHET, G. DURRY

J36 – *HIGH-RESOLUTION INFRARED SPECTROSCOPY OF $BrNO_2$ ISOTOPOMERS*
F. KWABIA TCHANA, J. ORPHAL, I. KLEINER, H. WILLNER, P. GARCIA, H.-D. RUDOLPH, B. REDLICH, O. BOUBA

J37 – *HIGH RESOLUTION FTIR STUDY OF THE COUPLED ν_2/ν_5 BANDS AND THE EQUILIBRIUM ROTATIONAL CONSTANTS OF $D_3Si^{35}Cl$*
E.B. MKADMI, H. BÜRGER

J38 – *FTIR MEASUREMENTS OF $^{12}C^{16}O_2$ LINE POSITIONS AND INTENSITIES OF HOT BANDS NEAR 2.7μm*
F. ANDRE, M.Y. PERRIN and J.TAINE

J39 – *NOBLE GAS - NOBLE METAL CHEMICAL BONDING? MICROWAVE SPECTRA AND GEOMETRIES OF KrCuF, KrCuCl, XeAgF AND XeAgCl*
STEPHEN A. COOKE, JULIE M. MICHAUD and MICHAEL C. L. GERRY

Invited Lectures K, Thursday, September 11, 9:00

Chairman : M. HERMAN

K1 – *EXPERIMENTS WITH QUANTUM DEGENERATE POTASSIUM-RUBIDIUM MIXTURES (45 min.)*
M. INGUSCIO

K2 – *PLANAR PLASMA EXPANSIONS AS A TOOL FOR HIGH RESOLUTION SPECTROSCOPY (20 min.)*
HAROLD LINNARTZ

K3 – *MILLIMETER WAVE SPECTROSCOPY OF HIGH RYDBERG STATES (20 min.)*
ANDREAS OSTERWALDER

Poster Session L, Thursday, September 11, 11:00

L1 – *COLD COLLISIONS WITH RYDBERG ATOMS*
ANDRÉ LUIZ DE OLIVEIRA, M. W. MANCINI, V.S. BAGNATO and L. G. MARCASSA

L2 – *CONTINUOS PRODUCTION OF HETERONUCLEAR COLD MOLECULES*
M. W. MANCINI, G. D. TELLES, A. R. L. CAIRES, V.S. BAGNATO and L. G. MARCASSA

L3 – *SPECTROSCOPY OF SINGLE CO MOLECULES IN ^{4}HE-DROPLETS*
KLAUS VON HAEFTEN, CARSTEN KRAUSE, STEPHAN RUDOLPH, ANDREAS RÜDIGER, MARTINA HAVENITH, IAROSLAV SIMANOVSKI

L4 – *HIGH-RESOLUTION SPECTROSCOPY OF METHANE IN PARAHYDROGEN CRYSTALS: CRYSTAL FIELD INTERACTION OF DEUTERATED SPECIES*
T. MOMOSE, H. HOSHINA, H. KATSUKI

L5 – *EPR SPECTRA AND ROTATION OF METHYL ISOTOPOMERS IN LOW TEMPERATURE MATRICES*
Yu. A. DMITRIEV

L6 – *REACTIVITY OF THE NITRIC OXIDE + METHYL CHLORIDE SYSTEM ISOLATED IN ARGON MATRIX*
L. KRIM, N. DOZOVA, AND N. LACOME

L7 – *A FREQUENCY ANALYSIS OF THE ν_9 BAND OF CD_3CD_3: EXPERIMENT AND AB INITIO CALCULATIONS*
A.C. SZOTT, J.R. COOPER, R.I. THOMPSON, A.R.W. McKELLAR, N. MOAZZEN-AHMADI

L8 – *AB INITIO STUDY OF ELECTRONIC STATES OF METAL-BENZENE MOLECULES*
F. RABILLOUD, A. R. ALLOUCHE, M. AUBERT-FRECON, R. ANTOINE, M. BROYER, I. COMPAGNON, P. DUGOURD, D. RAYANE

L9 – *AB INITIO CALCULATIONS ON THE SF_5Cl MOLECULE*
N. ZVEREVA, M. ROTGER, V. BOUDON and M. LOËTE

L10 – *COMPLEXES WITH INORGANIC HYDRIDES (NH_3, PH_3, AsH_3)*
N. A. ZVEREVA

L11 – *AB INITIO STUDY OF THE $NH_3 \cdots H_2$ COMPLEX – FIRST SADDLE POINT OF INDEX TWO ON A REACTION PATH*
R. M. MINYAEV, I. V. GETMANSKII, WOLFGANG QUAPP

L12 – *A SIMPLE APPROXIMATION TO VALLEY-RIDGE-INFLECTION POINTS ON POTENTIAL ENERGY SURFACES*
WOLFGANG QUAPP

L13 – *IMPROVED VARIATIONAL CALCULATIONS OF THE VIBRATIONAL ENERGIES FOR NH_3 FROM HIGH-LEVEL AB INITIO POTENTIAL ENERGY SURFACES*
HAI LIN, WALTER THIEL, SERGEI N. YURCHENKO, MIGUEL CARVAJAL and PER JENSEN

L14 – *A NEW SEMI-EMPIRICAL POTENTIAL FOR AR-CO*
GERHARD W. SCHWAAB, MARTINA HAVENITH

L15 – *THE ANALYSIS OF TEMPERATURE DISTRIBUTION IN AN END-PUMPED SOLID- STATE LASER FOR SPECTROSCOPIC APPLICATIONS*
H. NADGARAN, P. ELAHI

L16 – *A GENERAL METHOD TO GENERATE COLD RADICALS FOR STUDIES BY HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY: APPLICATION TO NH_2*
STEFAN WILLITSCH and FREDERIC MERKT, JOHN M. DYKE

L17 – *NUCLEAR SPIN CONVERSION IN ELECTRIC FIELD: THE ROLE OF COLLISIONS*
P. CACCIANI, J. COSLÉOU, F. HERLEMONT, M. KHELKHAL and J. LECOINTRE

L18 – *ROTATIONAL DEPENDENCE OF THE DIPOLE MOMENT OF CH_3F FROM THE MEASUREMENTS OF THE NUCLEAR SPIN CONVERSION SPECTRUM*
J. COSLÉOU, P. CACCIANI, F. HERLEMONT, M. KHELKHAL AND J. LECOINTRE, P. PRACNA

L19 – *INTERFACING THE ZURICH FTIR SPECTROMETER BRUKER IFS 120 HR (PROTOTYPE) WITH A COLLISONAL COOLING CELL*
SIEGHARD ALBERT, SIGURD BAUERECKER, MARTIN QUACK

L20 – *THE TIME RESOLVED IR-IR DOUBLE RESONANCE: A TOOL TO STUDY THE RELAXATION OF CH_4 MIXED WITH H_2, N_2, OR He AFTER EXCITATION INTO $2\nu_3$ AND TO DETECT NEW CH_4 HOT BAND LINES*
F. MENARD-BOURCIN, L. DOYENNETTE, J. MENARD, and C. BOURSIER

L21 – *SUBMILLIMETER-WAVE MEASUREMENTS OF THE PRESSURE BROADENING OF BrO, HO_2, AND O_3*
M. M. YAMADA, T. AMANO, B. J. DROUIN

L22 – *ABSORPTION PROFILES OF HCl FOR THE $J = 1 - 0$ TRANSITION: FOREIGN GAS EFFECTS MEASURED FOR N_2, O_2, AND Ar*
ISAMU MORINO, KOICHI M. T. YAMADA

L23 – *MODELING OF THE ROTATIONAL RELAXATION MATRIX IN LINE MIXING EFFECT CALCULATIONS*
A. V. DOMANSKAYA, N. N. FILIPPOV, N. M. GRIGOROVICH and M. V. TONKOV

L24 – *MODELING OF ABSORPTION IN CENTRAL AND WING REGIONS OF CO_2 IR BANDS. COMPARISONS WITH LABORATORY AND ATMOSPHERIC SPECTRA*
C. F. NIRO, J. M. HARTMANN, T. VON CLARMANN, F. HASE, K. W. JUCKS, and C. CAMY-PEYRET

L25 – *EFFECT OF DENSITY AND TEMPERATURE ON THE INFRARED SPECTRA OF FLUID ETHENE BY MOLECULAR DYNAMICS SIMULATIONS*
A. DECRETTE, and J.-M. SIMON

L26 – *EXPERIMENTAL AND SIMULATED INFRARED SPECTROSCOPIC STUDIES OF THE INTERACTION OF ETHYLENE ON A MFI ZEOLITE*
A. DECRETTE, V. BERNARDET, J. M. SIMON, O. BERTRAND, G. WEBER and J. P. BELLAT

L27 – *DIPOLE MOMENT CALCULATIONS AND STARK EFFECT STUDIES IN THE LOW-LYING STATES OF RbCs*
A. V. ZAITSEVSKII, E. A. PAZYUK, and A. V. STOLYAROV, O. DOCENKO, I. KLINCARE, O. NIKOLAYEVA, M. TAMANIS, and R. FERBER

L28 – *COMPARISON OF THE INSTANTON AND STANDARD WKB CONTRIBUTIONS TO TUNNELING SPLITTING SPECTRA OF FLOPPY MOLECULAR SYSTEMS*
GEORGE S. IROSHNIKOV , LEONID P. SUKHANOV

L29 – *ON THE DETERMINATION OF INTRAMOLECULAR POTENTIAL FUNCTION OF THE PH_3 MOLECULE*
O. N. ULENIKOV, O. L. KHABIBULINA, E. S. BEKHTEREVA, G. A. ONOPENKO

L30 – *HIGH RESOLUTION FOURIER TRANSFORM SPECTRUM OF PD_3 IN THE REGION OF THE STRETCHING OVERTONE BANDS $2\nu_1$ AND $\nu_1 + \nu_3$*
O. N. ULENIKOV, YU. B. YUHNIK, E. S. BEKHTEREVA, N. E. TYABAEVA, H. BÜRGER, W. JERZEMBECK, L. FUSINA

L31 – *OBSERVATION OF THE $\Delta v_{GeH} = 5$ STRETCHING VIBRATIONAL OVERTONE OF $H_3{}^{70}GeD$ BY ICLAS-VeCSEL TECHNIQUE. ROVIBRATIONAL ANALYSIS OF A PERTURBATION-FREE LOCAL MODE STATE*
M. LITZ, H. BÜRGER, Y. DING, E. BERTSEVA, A. CAMPARGUE

L32 – *HIGH RESOLUTION STUDY OF SOME DOUBLY EXCITED VIBRATIONAL STATES OF PH_2D: THE $\nu_1 + \nu_2$, $\nu_2 + \nu_5$, $\nu_2 + \nu_3$, AND $\nu_2 + \nu_6$ BANDS*
O. N. ULENIKOV, E. S. BEKHTEREVA, S. V. GREBNEVA, H. BÜRGER, W. JERZEMBECK , C. LEROY

L33 – *GLOBAL ANALYSIS OF CHLOROMETHANE : RECENT RESULTS INVOLVING THE REGION FROM 1900 to 2600 cm^{-1}*
A. NIKITIN, J.P. CHAMPION, H. BÜRGER

L34 – *THE ν_5 BAND OF CH_3CD_3: HIGH RESOLUTION SPECTRUM AND GLOBAL THREE-BAND ANALYSIS*
J.R. COOPER, A.R.W. McKELLAR, I. OZIER, N. MOAZZEN-AHMADI

L35 – *SUMMARY OF RECENT ANALYSES OF THE FIRST FOUR POLYADS OF METHANE*
M. LOËTE, J.-P. CHAMPION, O. ROBERT, J.-C. HILICO, V. BOUDON, S. TOUMI, L. R. BROWN

L36 – *DETAILED INVESTIGATION OF THE ICOSAD (1.3 – 1.5 μm) OF $^{12}CH_4$ AT HIGH-RESOLUTION: PRELIMINARY ANALYSIS OF THE $\nu_2+2\nu_3$ REGION*
V. BOUDON, M. LOËTE, M. HIPPLER, M. QUACK, M.REY

L37 – *HIGH RESOLUTION UV SPECTROSCOPY OF 4-DIMETHYLAMINOBENZONITRILE*
GRZEGORZ MYSZKIEWICZ, GIEL BERDEN, W. LEO MEERTS

L38 – *HIGH-RESOLUTION FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $C^4\Delta - X^4\Phi$ TRANSITION OF TiCl*
H. HERBIN, R. FARRENQ, G. GUELACHVILI, N. PICQUÉ, B. PINCHEMEL

L39 – *SASSI EXTRACTION OF UNDERLYING FEATURES IN HIGH RESOLUTION FTIR SPECTRA*
DON McNAUGHTON , CHRISTOPHER D. THOMPSON AND EVAN G. ROBERTSON

Poster Session M, Thursday, September 11, 20:00

M1 – *RIGID DIATOMIC MOLECULES IN A STRONG EXTERNAL FIELD*
K. M. T. YAMADA, S. C. ROSS

M2 – *KINETIC MODELING OF FEMTOSECOND DYNAMICS IN CURVE-CROSSING SYSTEMS*
NIKOLAI E. KUZ'MENKO, VADIM V. ERYOMIN, and YULIA YU. PAKHOMOVA

M3 – *CONTROLLING ROTATIONAL DYNAMICS OF MOLECULES BY PHASE-SHAPED FEMTOSECOND LASER PULSES*
M. RENARD, E. HERTZ, B. LAVOREL, O. FAUCHER

M4 – *FEMTOSECOND DEGENERATE FOUR-WAVE MIXING (DFWM) AND COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (CARS) IN CO_2 AND H_2*
SOTROPA C., BERNIER M., RENARD M., FAUCHER O., AND LAVOREL B, TRAN H, AND JOUBERT P

M5 – *ADIABATIC RAPID PASSAGE AND OTHER NONLINEAR SPECTROSCOPIC EFFECTS IN THE SPECTRA OF NITRIC OXIDE AND METHANE AT 5 μm*
G. DUXBURY, JAMES F. KELLY, THOMAS A. BLAKE

M6 – *RAPID PASSAGE AND POWER SATURATION EFFECTS IN PULSED QUANTUM CASCADE LASER SPECTROMETERS*
M. T. McCULLOCH, G. DUXBURY and N. LANGFORD

M7 – *CONTROLLING THE MOTION OF HYDROGEN MOLECULES*
T. P. SOFTLEY, S. R. PROCTER,, Y. YAMAKITA, F. MERKT

M8 – *A COBRA FT-MW SPECTROMETER WITH COAXIALLY ALLIGNED ELECTRODES FOR STARK-EFFECT APPLIED IN RESONATORS (CAESAR)*
MELANIE SCHNELL, DEIKE BANSER, and JENS-UWE GRABOW

M9 – *VIBRATIONAL ENERGY LEVELS AND POTENTIAL ENERGY SURFACE OF METHYL FLUORIDE*
S. A. MANSON and M. M. LAW

M10 – *LONG RANGE INTERACTION IN CALCIUM DIMER*
OLIVIER ALLARD, ASEN PASHOV, HORST KNÖCKEL, EBERHARD TIEMANN, OLIVIER DULIEU

M11 – *NEW EQUILIBRIUM PARAMETERS OF THE CO^+ MOLECULE: THE FIRST-NEGATIVE BAND SYSTEM ANALYSIS*
R. HAKALLA, R. KEPA, WOJCIECH SZAJNA AND M. ZACHWIEJA

M12 – *ROTATIONAL SPECTRA AND MOLECULAR FORCE FIELD OF TRANS-1-CHLORO-2-FLUOROETHENE*
GABRIELE CAZZOLI, CRISTINA PUZZARINI, ALBERTO GAMBI

M13 – *THE EMPIRICAL EQULIBRIUM STRUCTURE OF TRANS-GLYOXAL FROM EXPERIMENTAL ROTATIONAL CONSTANTS AND CALCULATED VIBRATION-ROTATION INTERACTION CONSTANTS*
R. WUGT LARSEN, B. NELANDER, F. PAWLOWSKI, F. HEGELUND, P. JØRGENSEN, J. GAUSS

M14 – *VARIATIONAL ENERGY OF THE GROUND STATE FOR ISOTOPIC MODIFICATIONS OF* H_2^+
A. Ya. TSAUNE, J.–L. TEFFO, M. P. D'YACHENKO, and S. I. FESENKO

M15 – *FOURIER TRANSFORM ABSORPTION SPECTROSCOPY OF HOD IN THE VISIBLE AND NEAR-INFRARED SPECTRAL REGIONS*
M. BACH, P.-F. COHEUR, S. FALLY, M. CARLEER, C. CLERBAUX and R. COLIN, A. JENOUVRIER, M.-F. MERIENNE, C. HERMANS and A.-C. VANDAELE

M16 – *FURTHER ANALYSIS OF THE NEAR INFRARED AND VISIBLE EMISSION SPECTRUM OF* H_2
D. BAILLY, O. PIRALI, and M. VERVLOET

M17 – *WATER LINE PARAMETERS IN THE NEAR INFRARED AND VISIBLE*
R.N. TOLCHENOV, J. TENNYSON, S.V. SHIRIN, N.F. ZOBOV, O.L. POLYANSKY, A.N. MAURELLIS

M18 – *FOURIER TRANSFORM ABSORPTION SPECTROSCOPY OF WATER VAPOUR IN THE VISIBLE AND NEAR INFRARED SPECTRAL REGIONS*
P.-F. COHEUR, S. FALLY, M. BACH, M. CARLEER, C. CLERBAUX and R. COLIN, A. JENOUVRIER, M.-F. MERIENNE, C. HERMANS and A.-C. VANDAELE

M19 – *HIGH-RESOLUTION VIBRATIONAL SPECTROSCOPY USING LASER DIFFERENCE-FREQUENCY SPECTROMETER*
W. CHEN, E. POULLET, R. BOCQUET, J. BURIE, D. BOUCHER

M20 – *ROVIBRATIONAL ANALYSIS OF THE* ν_1 *BAND OF* CF_3Cl *FROM SUPERSONIC SLIT JET DIODE LASER SPECTRA*
A. PIETROPOLLI CHARMET, P. STOPPA, P. TONINELLO, S. GIORGIANNI, S. GHERSETTI

M21 – *PYROLYSIS OF DEUTERATED PYRIDINE AND* PCl_3*: THE MILLIMETER-WAVE SPECTRUM OF* DC_5N
L. BIZZOCCHI and C. DEGLI ESPOSTI

M22 – *ROVIBRONIC STATES OF HCN*
GEORG CH. MELLAU

M23 – *ON THE GLOBAL QUANTUM NUMBERS IN THE HCN↔CNH MOLECULE*
DMITRII SADOVSKII, MARC JOYEUX

M24 – *SEMIEMPIRIC APPROACH FOR CALCULATION OF* H_2O *AND* CO_2 *LINE BROADENING AND SHIFTING*
N.N. LAVRENTJEVA, A.D. BYKOV, L.N. SINITSA

M25 – *INVESTIGATION OF THE ROTATION-VIBRATION OF H_2O ISOLATED IN SOLID RARE GASES. NUCLEAR SPIN CONVERSION AND MATRIX EFFECT*
X. MICHAUT, C. CANUEL, A.-M. VASSEROT, AND L. ABOUAF-MARGUIN

M26 – *BROADENING AND SHIFTING PARAMETERS FOR H_2O IN THE 3500-3650 CM^{-1} REGION*
KAREN KEPPLER ALBERT, D. CHRIS BENNER and V. MALATHY DEVI, MARY ANN H. SMITH, MICHAEL LOCK

M27 – *THE EFFECTS OF ROTATION, VIBRATION, AND TEMPERATURE ON COLLISIONAL PARAMETERS OF H_2O LINES*
ROBERT R. GAMACHE and JEAN-MICHEL HARTMANN

M28 – *ABSOLUTE LINE INTENSITIES IN THE $\nu_1+3\nu_3$ BAND OF $^{12}C_2H_2$ BY LASER PHOTOACOUSTIC SPECTROSCOPY AND FOURIER TRANSFORM SPECTROCOPY*
F. HERREGODTS, E. KERRINCKX, T. R. HUET, J. VANDER AUWERA

M29 – *USING FAST FOURIER TRANSFORM TO COMPUTE THE LINE SHAPE OF FREQUENCY-MODULATED SPECTRAL PROFILES*
LUCA DORE

M30 – *STUDY OF BROADENING AND SHIFT COEFFICIENTS OF H_2O BY H_2 AND He IN THE 1.4 μm REGION: EXPERIMENT AND CALCULATIONS*
V. ZENINARI, B. PARVITTE, D. COURTOIS, I. POUCHET, G. DURRY, N.N. LAVRENT'EVA, Yu. N. PONOMAREV

M31 – *OPTIMIZATION OF FTIR SPECTROMETER FOR INTENSITY MEASUREMENTS*
J. LEHTOMAA, V.-M. HORNEMAN, and S. ALANKO

M32 – *CALCULATING THE QUASI-BOUND RO-VIBRATIONAL STATES OF H_3^+*
JAMES MUNRO,JONATHAN TENNYSON, HAMSE Y. MUSSA

M33 – *VECTOR PARAMETRIZATION, PARTIAL ANGULAR MOMENTA AND POLYSPHERICAL COORDINATES IN MOLECULAR PHYSICS. APPLICATIONS TO INFRA-RED SPECTROSCOPY OF NON-RIGID SYSTEMS*
A. NAUTS, F. GATTI

M34 – *ON THE APPLICATION OF CANONICAL PERTURBATION TO MOLECULAR DYNAMICS*
D. SUGNY, A. KELLER, O. ATABEK, M. JOYEUX

M35 – *MICROWAVE SPECTROMETER WITH PHASE SWITCHING FOR MOLECULAR BEAM RESEARCHES OF ORGANOMETALLIC MOLECULES*
ELENA G.DOMRACHEVA, V.V.KHODOS, V.L.VAKS

M36 – *DOPPLER-LIMITED ROTATIONAL SPECTRUM OF THE NH RADICAL IN THE 2 THZ REGION*
SANDRA BRUENKEN, FRANK LEWEN, GISBERT WINNEWISSER, MARIE SIMECKOVA AND STEPAN URBAN

M37 – *TOWARD THE IDENTIFICATION OF THE SUBMILLIMETER WAVE SPECTRUM OF THE BROMOMETHYL RADICAL, CH_2Br*
S. BAILLEUX, P. DREAN, C. DUAN, M. GODON, M. BOGEY, Z. ZELINGER

M38 – *ROTATIONAL SPECTRUM OF BROMINATED RADICALS PRODUCED BY UV PHOTOLYSIS*
P. DREAN, C. DUAN, M. HASSOUNA, A. WALTERS, M. GODON, M. BOGEY and S. BAILLEUX

M39 – *FOURIER TRANSFORM MILLIMETER-WAVE SPECTROSCOPY OF HYDROCARBON RADICALS*
EUNSOOK KIM and SATOSHI YAMAMOTO

Invited Lectures N, Friday, September 12, 9:00

Chairman : M. HAVENITH

N1 – *SLIT-JET IR SPECTROSCOPY: FROM MOLECULAR CLUSTERS TO HYDROCARBONS (45 min.)*
DAVID J. NESBITT

N2 – *NON-RIGID MOLECULES: IT IS NOW POSSIBLE TO MODEL THEIR HIGH-RESOLUTION SPECTROSCOPIC DATA (45 min.)*
L. H. COUDERT

Poster Session O, Friday, September 12, 11:00

O1 – *HIGH-ACCURACY AB INITIO ROTATION-VIBRATION TRANSITIONS FOR WATER*
O. L. POLYANSKY, S. V. SHIRIN, N. F. ZOBOV, A.G. CSASZAR, P. BARLETTA, J. TENNYSON, D.W. SCHWENKE, P.J. KNOWLES

O2 – *AB INITIO DIPOLE MOMENT SURFACE FOR THE WATER MOLECULE*
R.N. TOLCHENOV, O.L. POLYANSKY, J. TENNYSON, A. CSASZAR, A.E. LYNAS-GRAY, J. VAN STRALEN, L.VISSCHER

O3 – *DOPPLER-LIMITED FTIR SPECTRUM OF THE $\nu_3(a')/\nu_8(a'')$ CORIOLIS RESONANCE DYAD OF $CHC\ell F_2$ OBTAINED WITH A NEW BRUKER IFS 120HR SPECTROMETER, AND COMPARISON WITH AB INITIO CALCULATIONS*
SIEGHARD ALBERT, HANS HOLLENSTEIN, MARTIN QUACK AND MARTIN WILLEKE

O4 – *AB INITIO STUDY OF THE GROUND AND LOW-LYING ELECTRONIC STATES OF COBALT DIHALIDES, CoX_2 (X=F, Cl, Br, I)*
VALERII V. SLIZNEV, NATALJA VOGT and JÜRGEN VOGT

O5 – *AB INITIO ANHARMONIC FORCE FIELS AND EQUILIBRIUM STRUCTURE OF CARBONYL CHLOROFLUORIDE*
J.DEMAISON, A. PERRIN, H. BÜRGER

O6 – *3-BUTENESELENOL : MICROWAVE SPECTRUM AND AB INITIO CALCULATIONS*
D. PETITPREZ, G. WLODARCZAK, J. DEMAISON, J.-C. GUILLEMIN, H. MØLLENDAL

O7 – *AB INITIO STUDY ON THE STRUCTURE AND DYNAMICS OF PHENYLACETYLENE AND DIPHENYLACETYLENE*
YOSHIAKI AMATATSU, YASUNORI HASEBE and MASARU HOSOKAWA

O8 – *SPECTROSCOPICALLY DETERMINED POTENTIAL ENERGY SURFACES OF WATER MOLECULE*
S. V. SHIRIN, O. L. POLYANSKY, N. F. ZOBOV, J. TENNYSON

O9 – *HIGH RESOLUTION SPECTROSCOPY OF BENZENE MOLECULE MEASURED BY THE COLLIMATED MOLECULAR BEAM AND ITS MAGNETIC FIELD EFFECT*
A. DOI, E. FURUI and H. KATÔ, M. BABA

O10 – *A SUPERSONIC JET SPECTROMETER FOR TERAHERTZ APPLICATION*
M. CARIS, G. FUCHS, P. NEUBAUER-GUENTHER, T. GIESEN, F. LEWEN, and G. WINNEWISSER

O11 – *OODR-STARK-SPECTROSCOPY ON JET-COOLED PENTACENE*
G. HOHEISEL, E. HEINECKE, A. HESE

O12 – *HIGH SENSITIVITY NEAR INFRARED SPECTROSCOPY OF PEROXY RADICALS IN SLIT SUPERSONIC EXPANSION*
ONDREJ VOTAVA

O13 – *HIGH-RESOLUTION SPECTROSCOPY OF THE $S_1 - S_0$ TRANSITION OF NAPHTHALENE IN A COLLIMATED MOLECULAR BEAM*
MASAAKI BABA, ATSUSHI DOI, EIJI FURUI, SHUNJI KASAHARA, and HAJIME KATÔ

O14 – *FOURIER TRANSFORM FREE-JET SET-UP FOR THE SPECTROSCOPIC INVESTIGATION OF VERY HOT GASES*
R. GEORGES, S.D. LE PICARD, S. CARLES, A. BENIDAR, and B.R. ROWE

O15 – *INVESTIGATION OF THE VIBRATIONAL ENERGY PATTERN IN THE DIMER OF FORMIC ACID*
R. GEORGES, M. FREYTES, D. HURTMANS, I. KLEINER, J. VANDER AUWERA, and M. HERMAN

O16 – *THE NO DIMER : ARE THE LIFETIMES OF THE ROVIBRATIONAL LEVELS, IN THE $V_5 = 1$ STATE, ROTATIONALLY DEPENDENT ?*
P. ASSELIN, P. SOULARD, AND N. LACOME

O17 – *POLARISATION LABELLING SPECTROSCOPY TECHNIQUE APPLIED TO HETERONUCLEAR ALKALI DIMERS: RECENT RESULTS FOR KLi, NaK AND NaRb*
A. GROCHOLA, P. KOWALCZYK, W. JASTRZEBSKI

O18 – *PECULIARITIES OF ATOM-DIATOM COLLISION COMPLEX FORMATION: CLASSICAL TRAJECTORY STUDY*
SERGEY V. IVANOV

O19 – *THE STUDY OF THE WATER–CARBON DIOXIDE COMPLEXES: FTIR SPECTROSCOPY IN VARIOUS MATRICES AND ANHARMONIC VARIATIONAL CALCULATIONS*
LUCE ABOUAF-MARGUIN, XAVIER MICHAUT, ANDRÉ SCHRIVER, LOUISE SCHRIVER-MAZZUOLI, ANATOLYI I. PAVLYUCHKO, ANDREI A. VIGASIN

O20 – *A SIMPLE ANALYTICAL PARAMETERIZATION FOR THE WATER VAPOR MILLIMETER WAVE FOREIGN CONTINUUM*
Q. MA, R. H. TIPPING

O21 – *ABSORPTION CROSS-SECTIONS OF FORMALDEHYDE BY FOURIER TRANSFORM SPECTROMETRY: UV-VISIBLE AND IR INTERCOMPARISON*
L. DAUMONT, A. JENOUVRIER, M.-F. MERIENNE, M. CARLEER, P.-F. COHEUR, R. COLIN, S. FALLY, M. KISELEVA, C. HERMANS, A.C. VANDAELE

O22 – *WEAKLY-BONDED COMPLEXES: HOW TO INTRODUCE SIMULTANEOUSLY QUANTUM INDIRECT DAMPING AND DAVYDOV COUPLING*
ADINA CEAUSU-VELCESCU, DIDIER CHAMMA, PAUL BLAISE, OLIVIER HENRI-ROUSSEAU

O23 – *VIBRATION AND ROTATION S-VECTORS, AND ROVIBRATIONAL HAMILTONIAN FOR FIVE ATOMIC MOLECULES OF A TYPE $XONY_2$*
ALEXANDER SKALOZUB, JAN MAKAREWICZ

O24 – *"EXACT" AND "PLANARITY-CONSTRAINED" KINETIC ENERGY OPERATOR FOR A MOLECULE OF MALONALDEHYDE*
ALEXANDER SKALOZUB, VLADIMIR ŠPIRKO

O25 – *A THEORETICAL STUDY OF THE ROVIBRATIONAL ENERGY LEVEL STRUCTURE IN THE GROUND ELECTRONIC STATE OF DIAZOCARBENE [CNN]*
VLADLEN MELNIKOV, TINA ODAKA, ROBERT J. BUENKER, PER JENSEN

O26 – *INVESTIGATION OF IMPURITIES OF TETRAFLUOROSILANE BY MICROWAVE GAS SPECTROSCOPY METHOD*
MARIYA.B.CHERNYAEVA, V.L.VAKS, E.G.DOMRACHEVA, N.V. KLYUEVA, P.G.SENNIKOV, L.A.CHUPROV

O27 – *MICROWAVE SPECTRUM AND INTRAMOLECULAR HYDROGEN BONDING IN 2- BICYCLOPROPYLIDENYLMETHANOL*
HARALD MØLLENDAL, SERGEJ I. KOZHUSHKOV, ARMIN DE MEIJERE

O28 – *MICROWAVE SPECTRUM AND STRUCTURE OF 1-THIA-CLOSO-DODECABORANE(11), 1-$SB_{11}H_{11}$*
HARALD MØLLENDAL, SVEIN SAMDAL, JOSEF HOLUB, DRAHOMIR HNYK

O29 – *UV-LASERSPECTROSCOPY ON 9-(CYANO)-ANTHRACENE*
ELKE HEINECKE, IAN MITCHELL, CHRISTIAN MONTE, WOLFGANG RETTIG

O30 – *UV-LASERSPECTROSCOPY ON 9-(N-CARBAZOLYL)-ANTHRACENE IN ELECTRIC FIELDS*
ELKE HEINECKE, MARKUS GLUGLA, IAN MITCHELL, CHRISTIAN MONTE, WOLFGANG RETTIG

O31 – *VACUUM-ULTRAVIOLET (10–27 eV) PHOTODISSOCIATION OF ETHYLENE ($H_2C=CH_2$) AND ALLENE ($H_2C=C=CH_2$) STUDIED BY FRAGMENT DISPERSED FLUORESCENCE*
K. ALNAMA, S. BOYE, S. DOUIN, D. GAUYACQ, F. INNOCENTI, J. O'REILLY, A. L. ROCHE, N. SHAFIZADEH, AND L. ZUIN

O32 – *THRESHOLD AND HIGH-FREQUENCY PECULIARITIES IN DIPOLE-BOUND ANION PHOTODETACHMENT*
B.A.ZON, V.E.CHERNOV

O33 – *INDUCED DIPOLE EFFECT ON PHOTODETACHMENT OF NEGATIVE IONS*
V.E.CHERNOV, B.A.ZON, HANSPETER HELM, IGOR YU. KIYAN

O34 – *FLUORESCENCE LIFETIMES OF THE $\overline{H}\ ^1\Sigma_g^+$ AND $R\ ^1\Pi_g$ STATES OF D_2*
KOICHI TSUKIYAMA

O35 – *SIMULATION OF HOT CARBON DIOXIDE SPECTRA*
VLADIMIR OSIPOV, NINA BORISOVA

O36 – *EMISSION SPECTRUM OF HOT D_2O IN 380–1800 CM^{-1}*
N. F. ZOBOV, S. V. SHIRIN, O. L. POLYANSKY, J. TENNYSON, A JANCA, K TERESZCHUK, P. F. BERNATH

O37 – *TEMPERATURE VARIATION OF THE CROSS-SECTION ABSORPTION BANDS OF OZONE IN THE 10000 TO 18500 CM^{-1} RANGE*
G. WANNOUS, Z. EL HELOU, E. BOURSEY, S. CHURASSY, B. ERBA, and R. BACIS, J. MALICET, and J. BRION

O38 – *INFRARED DIODE LASER SPECTROSCOPY OF THE CCO RADICAL: REGION OF THE C-C STRETCHING FUNDAMENTAL*
Z. ABUSARA, T.S. SORENSEN, N. MOAZZEN-AHMADI

O39 – *A HIGH-RESOLUTION FAR-INFRARED GAS PHASE SPECTRUM OF THE INTERMOLECULAR HCl LIBRATION BAND OF THE OC-HCl COMPLEX*
BENGT NELANDER, RENE WUGT LARSEN, FLEMMING HEGELUND

Invited Lectures P, Friday, September 12, 14:00

Chairman : P. R. BUNKER

P1 – *ORTHO-PARA TRANSITIONS IN H_2^+ (45 min.)*
I. R. MCNAB, I. GERDOVA and F. KEMP

P2 – *SPECTRA OF WATER IN THE HEAVENS AND ON EARTH (45 min.)*
JONATHAN TENNYSON

Invited Lectures A

Monday, September 8, 9:00

Chairman : M. QUACK

QUANTITATIVE ROTATIONAL SPECTROSCOPY FOR ATMOSPHERIC RESEARCH *(45 min.)*

G. WLODARCZAK , *Laboratoire de Physique des Lasers , Atomes et Molécules (UMR CNRS 8523) and CERLA, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq, France*

Remote sensing of rotational transitions in the Earth's atmosphere is one of the important methods to retrieve chemical composition profiles. In relation with recent or planned satellite programs (ODIN , EOS MLS, MASTER, SMILES), the last developments of laboratory works in the millimeter and submillimeter range will be presented. Various examples will be given including ozone, nitrous oxyde, methyl chloride. The determination of the lineshape parameters will be critically discussed. The departure of the observed lineprofiles from the Voigt profile will also be analyzed.

NEW FRONTIERS IN LASER SPECTROSCOPY *(45 min.)*

T. W. HÄNSCH, *Max-Planck-Institut für Quantenoptik, Garching, and Sektion Physik, Ludwig-Maximilians-Universität, München, Germany*

Femtosecond laser optical frequency combs are revolutionizing ultraprecise laser spectroscopy. At the same time, such comb synthesizers provide the long-missing "clockwork" for a new generation of optical atomic clocks. With sharp optical resonances in cold trapped ions, atoms, or slow molecules acting as the "pendulum" such optical clocks will further extend the limits of precision metrology and spectroscopy.

Laser Spectroscopy of the simple hydrogen atom has long yielded accurate values of important physical constants. Future experiments promise stringent tests of fundamental physics laws. They may unveil conceivable variations of fundamental constants or even differences between matter and antimatter.

Laser frequency comb techniques have also opened intriguing new opportunities in ultrafast physics. They make it possible to measure and control the evolution of the carrier-envelope phase of a mode-locked laser. With phase-controlled intense light pulses lasting only a few cycles, new phenomena are observed in nonlinear light-matter interactions. Recent experiments on high harmonic generation, above threshold ionization, and photoemission of a solid cathode will serve as illustrations.

Poster Session B

Monday, September 8, 11:00

ANALYSIS OF PHOSPHINE IN THE 3 μm REGION FOR PLANETARY APPLICATIONS

L. SAGUI, I.KLEINER, *Laboratoire de Photophysique Moléculaire ,Université Paris Sud, 91405 Orsay Cedex, France*; **R. A. H. BUTLER and L. R. BROWN**, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA*

Progress on the analysis of the high resolution spectrum of PH_3 in the 3 μm region between 2750 to 3600 cm^{-1} is reported. The objective is to provide line parameters for remote sensing of Saturn. For this, laboratory spectra have been recorded at a resolution of 0.012 cm^{-1} using the Fourier transform spectrometer located at the Kitt Peak Observatory. Using ground state combination differences, several hundred transitions have been assigned in $3\nu_2$, $2\nu_2 + \nu_4$, $\nu_2 + 2\nu_4$, $\nu_1 + \nu_2$, $\nu_3 + \nu_4$ and $\nu_1 + \nu_4$ centered around 2941, 3080, 3215, 3307, 3425 and 3432 cm^{-1} respectively. Analysis and preliminary modeling of the interacting energy states will be presented.[a]

[a]Part of the research reported in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology , under contract with the National Aeronautics and Space Administration.

SIMPLE, HIGHLY-MODULAR, MULTI-PLATFORM COMPUTER TOOLS FOR THE SIMULATION AND ANALYSIS OF HIGH-RESOLUTION RADIO-ASTRONOMICAL SPECTRA

A. KLOTZ, A. WALTERS, E. CAUX, *CESR - UPR CNRS 2592 and Université Paul Sabatier, 9 Avenue du Colonel Roche, TOULOUSE 31028 Cedex 4, France* ; **J. CROVISIER**, *LESIA, Observatoire de Paris - Meudon, 5 Place Jules Janssen, 92195 MEUDON Cedex, France*

Future instruments for submillimeter and FIR astronomy like the Herschel Space Observatory (planned launch 2007) and ALMA will offer the possibility to make high-resolution wide-frequency spectral surveys of the interstellar and circumstellar media. For the preparation of the HSO in particular there is an urgent need to create a versatile computer tool for the prediction of spectra to be measured in different types of astrophysical objects. The analysis of observations of these instruments for the research of new species and the determination of physical conditions of the objects studied will be greatly facilitated by the availability of programs allowing the comparison and fitting of observed and simulated spectra. Although a variety of different programs exist for modelling astrophysical spectra there is no general widely-available program specifically adapted to wide spectral scans. In order to allow for the wide-variety of differing conditions in the objects to be studied, the inherent complexity of certain astrophysical spectra (high spectral density and object-dependant lineshapes) these computer tools should be based on simple astrophysical models but with modular architecture permitting the permutation of different elements and the future addition of more sophisticated methods of analysis where warranted. As a first step we have rewritten using object oriented multi-platform algorithms a program (by Jacques Crovisier) for the prediction of cometary spectra to which has been added a graphical interface. The objective is to show how different modules such as templates for various objects and a choice simple of simple predictive calculations (thermal equilibrium, LVG, ...) could be added together to create an extremely versatile analysis tool for many types of astrophysical spectra.

We thank the French National Program PCMI for helping to support this work.

ABSORPTION SPECTROSCOPY OF JET-COOLED PAHS

O. SUKHORUKOV, A. STAICU, and G. ROUILLÉ,
Friedrich-Schiller-Universität, Helmholtzweg 3, D-07743 Jena;
F. HUISKEN and T. HENNING, *Max-Planck-Institut für Astronomie, Königstuhl 17, D-69117 Heidelberg*

The polycyclic aromatic hydrocarbons (PAHs) in either neutral or ionic form are expected in the Interstellar Medium[a] and are possible carriers for the Diffuse Interstellar Bands (DIBs).[b] In order to prove their presence and especially their relevance to the DIBs, the absorption spectra of these species must be measured in the laboratory under astrophysically relevant conditions, i.e., in the gas phase and at very low temperature. The matrix isolation spectroscopy (MIS) technique was used to obtain spectra under conditions close to those in space but they are affected by matrix shifts.[b] In order to obtain proper gas phase absorption spectra, we have chosen cavity ring-down spectroscopy (CRDS) in combination with the supersonic free jet expansion technique. Here we report the application of this technique to neutral PAHs, namely to the $S_0 \rightarrow S_1$ system of anthracene at 361 nm as well as to the $S_0(0) \rightarrow S_2(0)$ and $S_0(0) \rightarrow S_2(v_{a_g} = 1)$ transitions of pyrene at 321 nm and 316 nm, respectively. We stress the importance of obtaining direct absorption spectra instead of using indirect methods like laser-induced fluorescence as employed for these molecules by other authors.[c,d] It was demonstrated by Romanini et al.[e] and by Biennier et al.[f] that the CRDS technique is also applicable to positively charged PAHs. Therefore, we intend to extend our studies to PAH cations as well.

[1] G. P. van der Zwet and L. J. Allamandola, *Astron. Astrophys.* **146**, 76-80 (1985).
[2] F. Salama, G. A. Galazutdinov, J. Krelowski, L. J. Allamandola, and F. A. Musaev, *Astrophys. J.* **526**, 265-273 (1999).
[3] E. A. Mangle and M. R. Topp, *J. Phys. Chem.* **90**, 802-807 (1986).
[4] N. Ohta, H. Baba, and G. Marconi, *Chem. Phys. Lett.* **133**, 222-229 (1987).
[5] D. Romanini, L. Biennier, F. Salama, A. Kachanov, L. J. Allamandola, and F. Stoeckel, *Chem. Phys. Lett.* **303**, 165-170 (1999).
[6] L. Biennier, F. Salama, L. J. Allamandola, and J. J. Scherer, *J. Chem. Phys.* **118**, 7863-7872 (2003).

ONE MARTIAN YEAR OF THE ORBITING THERMAL EMISSION SPECTROMETER'S OBSERVATIONS OF THE 10μm CO_2 HOT BAND EMISSION

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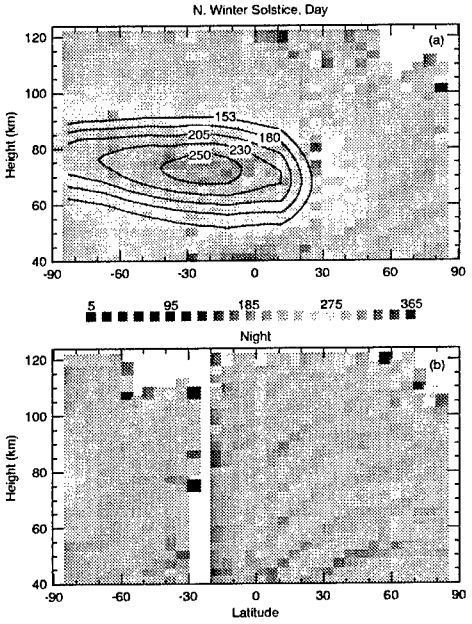
More than a complete Martian year's Mars Global Surveyor (MGS/TES) data have been obtained allowing tracking of the 10μm CO_2 hot band emission. We show the latitudinal and height changes of the emission as a function of time. Previously, we have shown how absorption of solar radiation in the 1-5μm region pumping the ν_3 CO_2 manifold in our non-LTE (non-local thermodynamic equilibrium) model reproduces the seasonal, latitudinal and height dependence of this IR emission. An example of our modeling, for northern winter solstice



is shown for day (in the upper panel) and night observations. The color bar defines the observed radiance index (1) while the contours are our theoretical

calculations. Other seasons' observations are similarly well fit(1). We will describe our model and discuss high altitude observations.

(1) W.C. Maguire, J.C. Pearl, M.D. Smith, B.J. Conrath, A.A. Kutepov, M.S. Kaelberer, E. Winter and P.R. Christensen, Observations of high-altitude CO_2 hot bands in Mars by the orbiting Thermal Emission Spectrometer,*J.G.R.* **107**(E), doi: 10.1029/2001JE001516, 2002.

CH_2CN^-: CARRIER OF THE 8037 Å DIFFUSE INTERSTELLAR BAND?

M. A. CORDINER, P. J. SARRE, *School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom*

A weak diffuse interstellar absorption band near 8037 Å observed in spectra of heavily reddened stars is tentatively attributed to a transition (A←X) from the electronic ground state to the first dipole-bound state of the cyanomethyl anion (CH_2CN^-). Rotational contour calculations based on high-quality data from high-resolution laboratory studies of CH_2CN^- by Lykke et al.[a] are compared with the 8037 Å diffuse band recorded along lines of sight towards the Galactic targets Cygnus OB2 #12, Cygnus OB2 #8a, HD 183143, and HD 229196. The data were recorded using the HIRES facility on the Keck telescope[b]. The computed Doppler-broadened contour is compared in detail with the 8037 Å diffuse band profile observed towards Cygnus OB2 #12 and shows good agreement within the current signal-to-noise limits. The CH_2CN^- rotational energy level populations are taken to be determined by the 2.7 K cosmic microwave background radiation field.

[a]Lykke, K.R., Neumark, D.M., Andersen, T., Trapa, V.J. and Lineberger, W.C., 1987, J. Chem. Phys. **87**, 6842

[b]Observations made by G. H. Herbig, 1997, private communication

TiO AND VO IN STELLAR AND CIRCUMSTELLAR ENVIRONMENTS

R. HUNTER, P. A. COUCH, J. McCOMBIE and P. J. SARRE,
School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

Bands of the refractory molecules TiO and VO are prevalent in the optical spectra of oxygen-rich stars and provide good probes of both stellar and circumstellar environments. Using line list data in conjunction with a radiative transfer treatment, including a new list developed for VO, we have modelled TiO and VO bands arising from absorption by material in photospheric and circumstellar regions. TiO and VO band simulations for the unusual object IRAS 08182-6000 show a high abundance of cool circumstellar gas phase molecules with rotational temperatures of *ca.* 300 K which is much lower than their condensation temperature. Possible reasons for their existence in the gas phase are discussed.

SUB-DOPPLER SPECTROSCOPY OF HYDROGEN AND DEUTERIUM CYANIDE ISOTOPOMERS

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MARIE SIMECKOVA AND STEPAN URBAN, *The J. Heyrovsky Institute of Phys. Chemistry, Dolejskova 3, CZ-18223 Praha 8, Czech Republic*

Rotational spectra of eight isotopomeres of the hydrogen (deuterium) cyanide ($H^{12}C^{14}N$, $H^{13}C^{14}N$, $H^{12}C^{15}N$, $H^{13}C^{15}N$, $D^{12}C^{14}N$, $D^{13}C^{14}N$, $D^{12}C^{15}N$, and $D^{13}C^{15}N$) have been measured using the Cologne mm- and submm-spectrometers in the frequency region from 70 GHz to 2 THz. The spectra up to 960 MHz have been mostly measured by the saturation dip sub-Doppler technique. The corresponding very high resolution (70 kHz) has made possible partly or completely to resolve underlying hyperfine structures due the ^{14}N nucleus. The hyperfine structures have been analyzed in terms of the effective electric quadrupole moment and magnetic nuclear spin rotation coupling parameters. The hyperfine structures due to ^{13}C, D, H, and ^{15}N isotopes have not been resolved but the corresponding saturation dips were significantly broader. The hyperfine free rotational frequencies together with the transition frequencies of unresolved rotational lines and with available precise rovibrational datas from previous measurements were subjected to a global least squares analysis to obtain rotational and centrifugal distortion parameters for each isotopomer. The calculated transition frequencies, including the hyperfine splitting, will be published in the Cologne internet Database for Molecular Spectroscopy (CDMS) at www.cdms.de.

The Cologne group has been supported by the Deutsche Forschungsgemeinschaft via research grants SFB-494. We kindly acknowledge the Ministry of Science of the Land Nordrhein- Westfalen/Germany for financial support. S.U. and M.S. acknowledge support through the Grant Agency of the Czech Republic (203/01/1274). The collaborative work between the Cologne and Prague groups has been additionally supported by the International Office of the Federal Ministry of Education and Science at the DLR via grant CZE 00/030.

OPTICAL PARAMETRICAL OSCILLATORS - A NEW LIGHT SOURCE FOR HIGH RESOLUTION SPECTROSCOPY

ANDREAS HECKER, MARTINA HAVENITH, *Physical Chemistry II, Ruhr University Bochum, D-44780 Bochum*

Continuous wave optical parametric oscillators are new and very powerful light sources for high resolution spectroscopy in the range between 0.4-4 μm. In order to cover the frequency range of the C-H, N-H and O-H- stretch vibration and reach high output powers a cw-opo based on a new concept has been set up. The new developed cw-opo uses a bow-tie cavity and is pumped by a master oscillator power amplifier system at 1064 nm. It covers the range between 2950-3900 nm with output powers up to 2.1 W. The nonlinear medium is a periodically poled lithium niobat crystal with 19 different gratings between 28.4-29.84 μm. We were able to show that the emission range is limited by the antireflection coating of the $LiNbO_3$ crystal. Therefore it is very easily possible to extend the frequency range by changing the $LiNbO_3$-crystal so that in the near future we will be able to cover the entire frequency region from 2 μm to 5 μm with this narrow linewidth and high power light source.

In order to demonstrate the capabilities of this new kind of opo-systems we used another cw-opo based on the same concept and covering the frequency range between 550-2830 nm with output powers of several hundred mW to measure the hyperfine structure of molecular iodine at 580 nm. Due to the fact that the measured linewidth of 2.5 MHz (HWHM) is dominated by pressure broadening a beat experiment between the opo-system and an all solid state laser was carried out to determine the real linewidth of the system, which is 20 kHz at a time 50 ms scale[a].

The poster shows the latest development in the field of optical parametrical oscillators and the newest spectroscopic results.

[a] A. Hecker et al. High resolution Doppler-free spectroscopy of molecular iodine using a continuous wave optical parametric oscillator Opt. Commun. 218 (1-3): 131-134 (2003)

DOPPLER-FREE TWO-PHOTON FLUORESCENCE EXCITATION SPECTROSCOPY AND THE ZEEMAN EFFECT OF THE 14_0^1 AND $14_0^1 1_0^1$ BANDS OF THE C_6D_6 $\tilde{A}\ ^1B_{2u} \leftarrow \tilde{X}\ ^1A_{1g}$ TRANSITION

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Doppler-free two-photon absorption of the $\tilde{A}\ ^1B_{2u}(v_{14} = 1$ and $v_{14} = 1,\ v_1 = 1) \leftarrow \tilde{X}\ ^1A_{1g}(v = 0)$ transitions of deutrated benzene C_6D_6 have been measured by two-photon fluorescence excitation spectroscopy with counter-propagating light beams of identical wavelength within an external cavity. The Zeeman effects were measured by applying a magnetic field perpendicular to the plane of linearly polarized laser beam (σ-pump). The experimental setup is almost the same with our previous report (J. Chem. Phys. **116**,162 (2002)). The Zeeman effects were found to be very useful to assign spectral lines. The Zeeman splittings for lines of a given J were observed to increase regularly with K and reach a maximum at $K = J$. This demonstrates that the magnetic moment lies along the c axis (perpendicular to the molecular plane). Abnormal energy shifts were observed for levels including those of $K = J$ at $J \geq 30$ in the $\tilde{A}\ ^1B_{2u}(v_{14} = 1)$ state. The Zeeman splittings of the perturbing lines were observed to be the same magnitude with the ones of the $\tilde{A}\ ^1B_{2u}$ state. The perturbation is identified as originating from a parallel Coriolis interaction. Much more lines were perturbed in the $\tilde{A}\ ^1B_{2u}(v_{14} = 1, v_1 = 1)$ state, but the many of lines could be assigned by referring the Zeeman spextrum.

DOPPLER-FREE POLARIZATION LABELING SPECTROSCOPY OF NAPHTHALENE MOLECULE

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Doppler-free laser polarization (DFLP) spectroscopy and Doppler-free optical-optical double resonance polarization labeling spectroscopy (DFOOPL) are applied to a large polyatomic molecule, naphthalene, at room temperature. Rotational resolved high-resolution absorption spectra of the 33_0^1 vibronic band of the $\tilde{A}^1B_{1u} \leftarrow \tilde{X}^1A_g$ electronic transition around 32453 cm^{-1} region have been measured and assigned. [a] The observed line width was about 15 MHz, and the absolute wavenumber was determined with an accuracy of 0.0002 cm^{-1}. DFLP spectroscopy is a very sensitive technique, and DFOOPL spectroscopy is a powerful tool for the unambiguous assignment for the complicated spectrum such as polyatomic molecule. By measuring V-type and Λ-type OODR transitions, we confirmed the assignment of the complicated lines in DFLP spectrum. As a results, more than 4600 lines in the range J=4-154 and K_a=0-40 were assigned. The molecular constants of the $\tilde{A}^1B_{1u}(v_{33} = 1)$ and $\tilde{X}^1A_g(v = 0)$ states were determined. In the present work, we demonstrate these spectroscopic techniques are very useful to investigate the electronic transition of polyatomic molecules.

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BROADBAND KILOMETRIC ABSORPTION PATH LENGTH SPECTRA IN THE 1.5 μm REGION

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The development of IntraCavity Laser Absorption Spectroscopy (ICLAS) in the infrared spectral range, despite its obvious benefits, has been hampered for long by a lack of availability of appropriate lasers and less efficient spectroscopic approaches. Indeed, lots of infrared lasers need cryogenic operation, or high pump power, or exhibit narrow gain profile, or only pulsed mode operation, and are available on restricted spectral areas. ICLAS has been demonstrated with lasers for instance such as KCl:Li F_a(II) color center laser[a], solid-state Co:MgF_2 laser[b] or rare-earth doped fibre lasers[c], but no systematic spectroscopic exploitation has been reported yet.

Recent progress in laser technology has generated new interest in sensitive spectroscopic experiments in the infrared, with the availability of tunable devices operating at room temperature, based on semiconductor or solid-state gain media. Among these, Cr^{4+}:YAG crystal[d] allows wide tunability in the 1.5 μm region and appears as an attractive candidate for ICLAS, as already demonstrated[e].

In this poster, the implementation of an intracavity absorption experiment with a Cr^{4+}:YAG laser[f] and a stepping-mode time-resolved Fourier transform interferometer is described. Preliminary results are given and discussed.

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HIGH-RESOLUTION LASER PHOTOACOUSTIC SPECTROSCOPY OF PH_3: THE FIFTH P-H STRETCHING OVERTONE BANDS

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The fifth P-H stretching overtone bands of phosphine are currently investigated. The spectrum was recorded at room temperature with a gas pressure of 116 hPa between 12 500 and 12 780 cm^{-1}.The spectrometer is a titanium:sapphire ring laser (Coherent 899-29) pumped by an Innova 400, 15 W argon-ion laser, which is coupled to a high sensitivity acoustic cell (α_{min} = 5x10^{-9} cm^{-1}) filled with gas. Most spectra were recorded with a laser power of 1.5 W, a time constant of 300 ms, and a typical sensitivity of 100-500 μV. The spectrum of phosphine has been recorded at room temperature with a gas pressure of 116 hPa between 12 500 and 12 780 cm^{-1}.

The Δv=6 spectrum is characterized by one band system centered at 12 678.2 cm^{-1}. It is assigned to the local mode P-H stretching (600 A_1/E) bands. The analysis started by locating the most intense $^rR_K(J)$ and $^pP_K(J)$ lines (with K=J) and the $^rQ_0(J)$ lines of the perpendicular band, using the ground state combination differences technique. The ground state constants were kept fixed to the values from the litterature (L. Fusina and G. Di Lonardo, *J. Mol. Struct.* 517-518 (2000) 67-78). Lines up to J=0-6 have been assigned. Last year a Hamiltonian model which makes use of simple arithmetic relations between some rovibrational parameters was used and a preliminary set of parameters was obtained. The molecular parameters seemed to confirm the local mode tendency of the PH_3 molecule in the near infrared range. We are now attempting to reach the experimental accuracy. A C_{3v} model is used to take into account the vibration-rotation perturbations.

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TRANSITION INTENSITIES IN H_3^+ AND ISOTOPOMERS

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There have been many experiments carried out on H_3^+ , both spectroscopically[a] and near dissociation[b,c]. However to date no measurements of the absolute transition intensities have been made; only relative intensities have been produced by experiment. Fárník *et al* [d] found that there were some anomalies between theory and experiment in the intensity data. A recalculation using more converged wavefunctions has shown no evidence that the problem was due to theory.

All applications for H_3^+ intensity data relies on *ab inito* calculations. Recently there has been a large demand from astrophysics for H_3^+ data, particularly for of the isotopomers H_2D^+ and D_2H^+ . These ions have completely different transition intensities as they have permanent dipole moments due to their asymmetry. This interest has been caused in part by the the recent observations of multiply deuterated species in the inter stellar medium[e,f]. The species are produced by deuterium fractionation effects[g].

Our overall aim is to explain the predissociation spectrum of the Carrington *et al* experiment[b,c]. The experiment found a very dense spectrum consisting of over 27,000 absorption lines in a region between 872cm^{-1} to 1094cm^{-1} . This experiment has remained largely unexplained since is was carried out over 20 years ago. In order to produce calculated dissociating intensities in this region, high lying wavefunctions will need to be converged. This will require the use of optimized methods, which will minimise the computational work of any calculation. In addition massively parallel computers such as HPCx will be needed.

A method of calculating the line strengths of the H_3^+ spectrum will be outlined, including optimization techniques. These include discrete variable representation of the wavefunction, use of symmetry and an algorithm for massively parallel calculations.

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ACETYLENE AS A HYDROGEN BOND DONOR: VIBRATIONAL SPECTRA AND DYNAMICS OF ISOLATED CLUSTERS

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It is well known that the C-H group of acetylene and other alkynes can bind to various inorganic and organic bases with lone pairs. This type of interactions can be classified as weak hydrogen bonds. The vibrational dynamics of such clusters has been studied mostly in rare gas matrices[a] and in solution[b], whereas only a few high resolution studies of mixed dimers are known[c]. Using the ragout-jet FTIR approach[d], we have obtained cluster spectra of acetylene with ammonia, acetone, ethylacetate, diethylether, eucalyptol, and other O- and N-bases in the CH and CC stretching region. The results are discussed in the context of dimer and trimer formation, hydrogen bond induced frequency shifts, and CC stretch intensity enhancement due to symmetry breaking. Extensive quantum-chemical calculations using GAUSSIAN and MOLPRO packages, in particular for the acetylene-ammonia dimeric system, are presented. Progress on complexes of other alkynes will also be reported.

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A NOVEL APPROACH TO THE ANALYSIS OF THE RYDBERG SPECTRA OF HCO

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Multi-Channel Quantum Defect Theory (MQDT) was used to simulate the photoionisation spectrum of HCO involving autoionizing Rydberg states in the region between the $v_2^+ = 2$ and $v_2^+ = 3$ threshold limits. This simulation is compared with our own experimentally recorded spectrum of resonances converging to the (03^10) state of HCO^+ observed from the photoselected $3p\pi\ ^2\Pi$ (030) $K' = 0, N' = 0$ intermediate state. (The notation $(v_1^+, v_2^{+K^+}, v_3^+)$ is used to describe the vibrational states of HCO^+). Second-photon excitation from first-photon prepared $3p\pi\ ^2\Pi$ (030) Σ^- $N' = 0$ promotes strictly R-branch transitions to vibrationally autoionizing high-n Rydberg states with total angular momentum excluding spin of $N = 1$ converging to various rotational states $N^+ = 1, 2, 3$...of HCO^+ (03^10). We were also able to simulate spectra converging to lower vibrationally excited HCO^+ ionization limits. We compare these simulations with those spectra recorded by Grant et al[1,2,3].

MQDT incorporates all channel interactions of the system into a short-range electronic quantum defect matrix and requires only the quantum defects and transition dipole moments as input parameters. A frame transformation is required to connect the Hund's case (d) channels appropriate for the long-range region into the eigenchannel basis appropriate for the close-coupled region, which is approximately Hund's case (b). Molecular symmetry group arguments are used to define which channels must be included in the quantum defect matrix. Spectroscopic studies of the $3p\pi$ state by Song & Cool[4] provide values for the $p\pi$ quantum defect for different values of v_2. Other quantum defects were estimated from those used in Rydberg simulations by Grant et al. Off-diagonal matrix elements were included to account for all possible interactions between channels, assuming s/d mixing to be negligible. A good agreement between experiment and theory is obtained by optimization of both the diagonal and off-diagonal matrix elements.

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ISOTOPE EFFECTS AND BORN OPPENHEIMER BREAKDOWN IN EXCITED SINGLET STATES OF THE LITHIUM DIMER

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Optical-Optical double resonance excitation of the F $^1\Sigma_g^+$ state of Li_2 (both $^6Li_2$ and $^7Li_2$ isotopomers) produces fluorescence to the A $^1\Sigma_u^+$ and B $^1\Pi_u$ states, and also collisionally induced systems in both the singlet and triplet manifolds. This work investigates the 1 $^1\Delta_g$ state, which correlates with the $Li(2p)^2P_{3/2}$ + $Li(2p)^2P_{3/2}$ atomic limit, observed in ten bands of the 1 $^1\Delta_g$ $\rightarrow$ B $^1\Pi_u$ system, occurring around 8500 cm^{-1}. The selective excitation of the F $^1\Sigma_g^+$ state populates either an a or an s rotational level. Since this nuclear spin symmetry is conserved in emission and collisional processes, line parities in the collisional system were readily deduced.

Determination of the Born-Oppenheimer breakdown parameters required an extensive data set linking all states with the electronic ground state. We recorded part of the B-X transition in absorption for the $^6Li_2$ system, at Doppler limited resolution, and took high resolution excitation data from the literature[a] for the same system in $^7Li_2$ and $^6Li^7Li$. The 1 $^1\Delta_g \rightarrow$ B $^1\Pi_u$ systems were recorded at a resolution of 0.06 cm^{-1} for both isotopomers (data for $^6Li_2$ has already been reported[b]). Data were fitted to Dunham-type polynomial expansions, with the ground state parameters taken from a study of Born-Oppenheimer breakdown in the A $^1\Sigma_u^+$ - X $^1\Sigma_g^+$ system of the lithium dimer[c]. The non-Born-Oppenheimer terms are found to be small but significant in this non-hydride molecule (the ^6Li and ^7Li atomic transitions $Li(2p)^2P_{3/2} \leftarrow Li(2s)^2S_{1/2}$ differ by 0.3 cm^{-1}).

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LATTICIES OF QUANTUM NUMBERS AND THEIR DEFECTS

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Attribution of approximate quantum numbers to observable molecular states is one of the most important step in understanding and interpretation of intramolecular dynamics and various molecular properties. Getting a system of quantum numbers means that approximate integrable model is constructed and locally quantum states form a regular lattice labelled by a system of several independently varying integers.

The aim of the present paper is to bring attention to the relation between defects of regular lattices and the Hamiltonian monodromy, which is a qualitative feature of classical integrable systems, responcible for the absence of global action-angle variables in classical mechanics and for the absence of global single-value system of labels of states in quantum problem. Analysis of the manifestation of classical Hamiltonian monodromy in quantum systems in general and in atomic and molecular systems in particular becomes recently a popular subject for both mathematical and physical studies (see [1-4] and references therein).

Integrable approximations to effective Hamiltonians with two degree of freedom possessing monodromy are studied from the point of view of classical and quantum mechanics. The joint spectrum of two commuting observables (energy and second integral of motion, like angular momentum, number of vibrational quanta, etc) is analysed in order to show the presence of defects of regular lattice of quantum states, associated with dynamical systems possessing Hamiltonian monodromy. The elementary monodromy defect is introduced, [5] which is related with the so-called focus-focus singularity of integrable Hamiltonian systems. In the case of dynamical systems with many focus-focus singularities the global monodromy is related with elementary ones and the corresponding defects are constructed. In particular, rotational dislocations of regular lattices are represented as a cumulative effect of several elementary monodromy defects.

Fractional monodromy, introduced in [6], is associated with specific line defect. The geometric way of constructing fractional line defect, characterised by a given fractional monodromy is suggested.

Manifestation of Hamiltonian monodromy in simple model effective Hamiltonians related to ro-vibrational, vibronic, and Rydberg state structure is discussed. The correspondence between monodromy and the reorganization of

energy bands in molecules under variation of some control parameters is suggested as one of the most interesting aspects of the manifestation of Hamiltonian monodromy in molecular systems.

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QUALITATIVE ANALYSIS OF CENTRIFUGAL EFFECTS IN ROTATIONAL SPECTRA OF NEARLY SYMMETRIC TOPS

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The influence of asphericity and centrifugal distortion on the rotational energy spectrum of $XY_3(C_{3v})$ type molecules is studied on the base of topological and symmetry analysis. In the case of XY_3 molecules with small $\gamma = \frac{C_e - B_e}{(C_e + B_e)/2}$ (asphericity equilibrium constant) the centrifugal deformation can significantly change the internal structure of rotational multiplet under rotational excitation, i.e. under increase of absolute value of rotational angular momentum J. Internal structure of J-multiplet can become more similar to spherical top multiplet which is characterized in high J-limit by the presence of 6-fold and 8-fold clusters.

The qualitative structure of the rotational multiplets is studied through the analysis of classical limit for model quantum ro-vibrational Hamiltonian taking into account simple harmonic force field. Rotational energy surface for the ground vibrational state is analyzed as a function of rotational equilibrium constants (γ-parameter), force field, rotational excitation $|J|$. In the limit of large asphericity the system of stationary points of rotational energy surface include three groups of isolated points with local stabilizers C_{3v}, C_s and C_2. These groups consist respectively of two, six and six equivalent by symmetry points. Stationary points with C_{3v} and C_2 stabilizers are fixed by symmetry whereas C_s isolated points are not fixed and move in the symmetry planes along with variation of parameters of the system, in particular, with $|J|$ excitation. When the centrifugal distortion effects become comparable with asphericity, new stationary points appear in the same planes C_s. Six new equivalent points are stable and six others are unstable. These points always remain in the plane of symmetry but their positions vary as J changes. For quantum system (in the limit of high values of J) this bifurcation corresponds to appearance of new 6-fold clusters in J-multiplet what can be interpreted as a quantum bifurcation.

So, qualitative modifications of the system of rotational energy levels in quantum multiplet are predicted on the base of the analysis of classical analog of quantum Hamiltonian. Typical sequence of rotational bifurcations corresponding to modifications of internal structure of multiplets between oblate and prolate top limits is constructed and represented on the correlation diagram relating oblate and prolate symmetric top with spherical top limit. All the results obtained in this work are tested on the molecules PH_3, AsH_3, SbH_3, BiH_3.

A NEW SCHEME OF K-LABELING FOR TORSION-ROTATION ENERGY LEVELS IN LOW-BARRIER MOLECULES

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A partially computer automatable labeling scheme for assigning K quantum numbers to torsion-rotation energy levels in low-barrier molecules is presented. It is based on a modification of the concept of overlap integrals between torsion-rotation eigenfunctions of adjacent J values. The scheme is rather simple and does not require any information other than that provided by the numerical eigenvectors obtained after diagonalization of the torsion-rotation Hamiltonian matrix. It was successfully applied to the K-labeling problem of both prolate (CH_3CHO) and oblate (CH_3CONH_2) type rotors with significant torsion-rotation interactions in their spectra. The scheme allows to give correct K-labels for eigenvectors in the majority of cases. The problems with the remaining cases are mainly caused by avoided crossings and may be fixed in a manual mode using a graphical visualization of the torsion-rotation energy level pattern[a].

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MILLIMETER-WAVE SPECTRUM AND GROUND STATE CONSTANTS OF METHYLAMINE

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We present recent progress that has been achieved in measuring and understanding the millimeter wave spectrum of the ground torsional state of methylamine (CH_3NH_2). The new measurements of the methylamine spectrum have been carried out in the 50 - 330 GHz frequency range using the Kharkov millimeter and submillimeter wave spectrometers[a]. The accuracy of measurements is estimated to be 0.010 MHz in the 50 - 150 GHz frequency range and 0.1 MHz above 150 GHz. The analysis of hyperfine structure of rotational lines due to quadrupole coupling has been done and hyperfine free data have been obtained. These data were combined with far-infrared data from [1] and submillimeter wave data from [2]. The analysis was carried out using the theoretical formalism presented in [3]. As a result a global fit of 553 microwave and 1407 far-infrared transitions was carried out yielding a weighted root mean square deviation of 0.736. The rms deviations of 0.020 MHz for microwave data and 0.00049 cm^{-1} for far-infrared data represent significant improvement in comparison with previous fits [1,2].

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MILLIMETER WAVE SPECTRUM OF ACETAMIDE

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We report recent progress in measuring, assigning and fitting the millimeter wave rotational transitions of the ground and first torsional states of the acetamide molecule CH_3CONH_2. The new meaurements of the acetamide spectrum have been carried out between 50 and 150 GHz using the microwave spectrometer in Kharkov[a]. We have assigned 427 and 231 new rotational transitions belonging to the A and E species, respectively, and involving J up to 20 and K_a up to 10. The observed spectrum of this low-barrier molecule was analyzed using the rho axis method (RAM), which was applied in the past to several internal rotors with success. After having removed the observed hyperfine splittings due to the quadrupole coupling, these new data along with 115 previously published measurements were fitted using 38 parameters of the RAM Hamitonian to give an overall weighted standard deviation of 1.05 for 630 lines belonging to the ground torsional state and 143 lines belong to the excited torsional state. Separate rms deviations for the A (34 kHz) and E (43 kHz) species, as well as for the $v_t = 0$ state (35 kHz)and the $v_t = 1$ state (48 kHz) indicate a similar quality of the fit for the two symmetry species and for the two torsional states. Earlier difficulties in the assignment process associated with finding the correct K label for higher-energy eigenvectors have been solved for the moment by a partially computer-automated labeling scheme (presented in a separate poster at this meeting by VVI) based on a modification of the concept of overlap integrals between torsion-rotation functions with adjacent J values.

[a]The millimeter wave measurements were supported by STCU under contract 2132

MICROWAVE SPECTRUM AND CONFORMATIONAL ANALYSIS OF TWO CONFORMERS OF JET-COOLED ETHYL ACETAMIDOACETATE, A PEPTIDE MIMETIC

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Rotational spectra of two conformers of the dipeptide mimetic, ethyl acetamidoacetate, were measured using the molecular-beam Fourier-transform microwave spectrometer at NIST. In each conformer internal rotation of the acetyl methyl group gives rise to observable splittings in the spectrum. Approximately 150 A species lines and 200 E species lines were analyzed for each conformer, using 15 and 18 torsion-rotation parameters, respectively, for the higher and lower symmetry conformers (see below), and yielding root-mean-square residuals of 1.8 kHz. From analysis of the torsion-rotation interactions, the orientation of the methyl group has been determined in the principal axis frame for each conformer, which permits an unambiguous identification of their conformational forms. One conformer exists in the all-trans configuration and belongs to the C_s point group. The other, a higher energy conformer, has C_1 symmetry. Two separate theoretical fitting procedures (one based on a global fit, the other on a perturbation treatment) were used to assess the reliability of the structural information, and the two procedures are shown to be essentially equivalent. The predicted energy ordering of these two conformers at the MP2/6-31G(d,p) level of theory is in disagreement with experimental observations.

MILLIMETER-WAVE SPECTROSCOPY OF NC_4P

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The unstable NC_4P molecule has been detected among the numerous products formed by copyrolysis of phosphorus trichloride and ortho-cyanotoluene. The amount of NC_4P produced is small, but sufficient to perform a systematic investigation of the millimeter-wave spectra for the ground and several excited bending states lying below 400 cm^{-1}, for which centimeter-wave data were already available.[a] The l-type resonances between the different sublevels of the bending states investigated, namely (v_8,v_9) = (0,1), (0,2), (0,3), (0,4), (1,0), and (1,1), have been taken into account in the analysis of the spectra, which yielded accurate determinations of the $x_{L(99)}$ and $x_{L(89)}$ anharmonicity constants. Transitions frequencies up to 420 GHz ($J = 241 \leftarrow 240$) were measured for the ground-state spectrum, making the evaluation of the sextic centrifugal distortion constant possible. Further pyrolysis experiments have shown that the yield of NC_4P can be greatly improved if the aromatic precursor is replaced by cyclopropyl cyanide. New measurements aiming at the assignment of the rotational spectra in excited vibrational states of higher energy are currently in progress.

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OPTIMAL STRATEGIES FOR REPRESENTING DIATOMIC MOLECULE DATA SETS

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Spectroscopic data reduction has three objectives: (i) to yield a compact representation of data sets which could include multiple-isotopmer data of different types (microwave, infrared, electronic, fluorescence series, tunneling linewidths) and consist of many tens of thousands of lines, (ii) to provide a practical means of interpolating for missing data within the range of the data set, (iii) to provide a means of extrapolating to predict unobserved data beyond the range of the existing data, and (iv) to yield molecular parameters of physical significance and allow us to predict other spectroscopic properties or other physical phenomena for that system.

Parameter-fit methods of addressing this problem include: (a) determining an empirical set of band constants $\{K_m(v)\} = \{G_v,\ B_v,\ -D_v,\ H_v,\ \ldots\}$ for each vibrational level of each isotopomer, (b) determining a set of Dunham $\{Y_{l,m}\}$ parameters, (c) using "near-dissociation expansions" (NDE's) instead of Dunham polynomials to represent the vibrational dependence of G_v, B_v and centrifugal distortion constants, and (d) using Dunham or NDE functions to represent G_v and B_v while constraining the centrifugal distortion constants to have the "mechanically consistent" values implied by the RKR potential energy function generated from those G_v and B_v functions. *Direct Potential Fit* methods perform exact quantum simulations of the data and fit to determine parameters describing an accurate analytic potential function for each electronic state. The strengths and weaknesses of these methods, and their relative effectiveness in addressing the four basic objectives presented above will be reviewed. New techniques which yield more effective parameter-fit representations of ordinary vibration-rotation data which span most of a potential well, and for the treatment of Λ–doubling splittings will be described.

STUDY OF THE MILLIMETER-WAVE SPECTRA OF THE LOWEST VIBRATIONAL STATES OF 1,1,1-DIFLUOROCHLOROETHANE

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The stratospheric ozone-depleting potential of chlorofluorocarbons (CFCs) has lead to their being phased out under the Montreal Protocol. Hydrochlorofluorocarbons (HCFCs) such as 1,1,1-difluorochloroethane are important transitional replacements, although they too are ozone depleters and will ultimately be eliminated. The possibililty of using IR spectroscopy for monitoring makes it desirable to thoroughly characterize the spectroscopy of this molecule.

About 80000 MMW absorption transitions of $CH_3CF_2{}^{35}Cl$ and $CH_3CF_2{}^{37}Cl$ were measured in the 55 - 150 GHz frequency range with an accuracy of about 20 kHz. More than 44000 transitions have been assigned. They belong to the ground, $18^1, 17^1, 11^1, 17^1+18^1, 11^2, 18^2, 9^1, 11^1+18^1, 11^1+17^1, 16^1$, and 10^1 states of $CH_3CF_2{}^{35}Cl$ and the ground, $18^1, 17^1, 11^1, 17^1+18^1$, and 11^2 states of $CH_3CF_2{}^{37}Cl$. Rotational, quartic, and sextic centrifugal distortion parameters as well as quadrupole coupling ones have been determined.

Two pairs of vibrational levels are found to be coupled by Coriolis interactions, namely, 10^1 with 16^1, and 9^1 with 11^1+18^1. The present results also resolve a disagreement in the literature about whether the band origin of the lowest 18^1 vibrational state is around 246 cm^{-1} or 272 cm^{-1}. Our fitting gives an energy difference between the 9^1 and 11^1+18^1 states of less than 1 cm^{-1}. The close proximity rules out 272 cm^{-1} for the origin of ν_{18} as it would imply a much greater separation of around 30 cm^{-1}. Moreover, the high resolution FTIR spectra recorded in Wuppertal by Prof. H. Burger contains a weak feature near 248 cm^{-1} that is assumed to be the ν_{18} band. No absorption was found in the vicinity of 272 cm^{-1}. Ab initio calculations at the MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels were also performed. Scaling of the ν_{18} torsional mode by comparison with 8 other CH_3-CXYZ fluorocarbons molecules leads to predictions of 239 cm^{-1} and 246 cm^{-1} at the B3LYP and MP2 levels. The fitted Coriolis interaction parameters between 10^1 and 16^1 (Z_a=0.093, Z_b=0.340) agree well with those predicted by the MP2/6-311+G(d,p) harmonic force field (Z_a=0.097, Z_b=0.352). Also it was

found that quadrupole splittings of the rotational transitions in the strong perturbed 10^1 and 16^1 states were not the same as in the unperturbed vibrational states.

We wish to thank Prof. H. Burger for the measured FTIR spectra.

THE HIGH RESOLUTION INFRARED SPECTRA OF ISOXAZOLE AND A COMPARISON WITH THEORETICAL STUDIES

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The high-resolution infrared spectrum of isoxazole has been obtained at room temperature, while those of isothiazole and its C-methyl derivatives form part of this project. A number of the isoxazole bands have been analysed, and provisional assignments of symmetry given. Two out-of-plane modes have been identified at 764 and 889 cm^{-1}. The results are compared with microwave spectral data, and especially with ab initio calculation of band position and intensity, at both the MP2 and CCSD(T) level of theory. These harmonic frequencies are obtained at the equilibrium structures, which are themselves compared with experimental microwave and other data. The 'molecular properties' determined at these structures include the dipole moment, and ^{14}N and ^{33}S nuclear quadrupole coupling constants known experimentally in the inertial axis frame, but are here converted to the electric field gradient principal axis framework.

ANALYSIS OF HIGH RESOLUTION FTIR SPECTRA OF $CH_2{}^{79}Br^{35}Cl$. THE ν_4 AND ν_5 FUNDAMENTALS AND THEIR HOT-BANDS $\nu_4+\nu_6-\nu_6$ AND $\nu_5+\nu_6-\nu_6$

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Bromochloromethane is a near prolate asymmetric rotor (κ = -0.991), occurring in four isotopic varieties ($CH_2{}^{79}Br^{35}Cl$, 38.22 %, $CH_2{}^{81}Br^{35}Cl$, 37.31 %,$CH_2{}^{79}Br^{37}Cl$, 12.38 % and $CH_2{}^{81}Br^{37}Cl$, 12.09 %). For the measurements reported here, a sample of isotopically enriched (^{79}Br) bromochloromethane was used. High resolution FTIR spectra were recorded in Wuppertal, by courtesy of Prof. Hans Bürger, at a nominal resolution of 0.0023 cm^{-1}, FWHM. Here we report the analysis of the ν_4 and ν_5 fundamentals of $CH_2{}^{79}Br^{35}Cl$, both A type bands with a negligible B-type contribution. The assignments were performed by using a Loomis-Wood program in combination with Ground State Combination Differences. The GSCD's performed well for low quantum numbers but the ground state constants had to be refined for higher J and K. Both fundamentals are essentially unperturbed and about 3000 transitions for each band could be fitted to Watson's Hamiltonian in the S-reduction, producing accurate ground state and excited state constants. A computer simulation of both bands showed an excellent agreement with the experimental spectra and by subtracting the simulation from the experimental data, a difference spectrum was generated, containing mainly features belonging to the fundamentals of the $CH_2{}^{79}Br^{37}Cl$ species and hot-bands of $CH_2{}^{79}Br^{35}Cl$. By applying Loomis-Wood and GSCD's to the difference spectrum, many transitions of the hot-bands starting from the lowest vibrational level, ν_6, at about 230 cm^{-1}, could be unambiguously assigned and fitted. In this way accurate molecular constants of the ν_6 state could be determined. The spectral structure of the ν_4 and ν_5 bands of $CH_2{}^{79}Br^{37}Cl$ was heavily obscured by the other, stronger bands, and only an estimate of the band origins was possible.

DIODE LASER SLIT JET SPECTRA AND ANALYSIS OF THE ν_{14} FUNDAMENTAL OF 1,1,1,2-TETRAFLUOROETHANE (HFC-134a)

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High resolution infrared spectra have been measured for mixtures of 1,1,1,2-tetrafluoroethane in Ne, expanded in a supersonic planar jet. The ν_{14} fundamental is an essentially unperturbed C-type band, exhibiting many $\Delta K_c = \pm 2$ transitions. Accurate excited state rotational and distortion constants have been determined from an analysis of about 1250 transitions, by using Watson's Hamiltonian in the S-reduction. A local perturbation has been observed with a crossing at $K'_a = 11$ for J'-values between 17 and 18, and could be accounted for by a x-Coriolis interaction with a perturbing vibrational level of A' symmetry at about 1205.53(1) cm^{-1}. Due to the very efficient cooling in the jet, the rotational temperature resulted to be about 20 K, and no evidence of hot-band absorption was found.

INFRARED LASER SPECTRUM OF THE P=O (ν_2) FUNDAMENTAL BAND OF CIS–HOPO

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The P=O (ν_2) stretching mode of the transient molecule *cis*-HOPO has been measured using high resolution infrared diode laser absorption spectroscopy. The molecule was formed by reacting white phosphorus vapour and the products of a microwave discharge through a mixture of hydrogen and oxygen in a flow system consisting of a multiple pass cell. Over 300 lines between 1242 cm^{-1} and 1267 cm^{-1} have been assigned. The band has the structure of an a-type transition of an asymmetric rotor. More than half of the assigned lines were included in a least squares fit using Watson's *A*-reduced Hamiltonian. The rotational constants are in satisfactory agreement with those predicted by Density Functional Theory and with those expected from a comparison with the nitrogen analogue, *cis*-HONO. The ground state constants are also closely similar to those from an earlier analysis of the ν_4 fundamental. The band origin is 1258.540 cm^{-1}. Many of the remaining, unfitted lines are perturbed, particularly around $K_a = 7$. The vibrational levels which are possibly responsible for this perturbation are also discussed.

ANALYSIS OF $D_2^{16}O$ EMISSION SPECTRUM IN THE 320 - 860 cm^{-1} SPECTRAL RANGE

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The emission spectra of pure D_2O sample were recorded in the 320-520 cm^{-1} spectral region at 1520 and 1950 K with different pressures (1, 14, and 16 torr) and resolutions (FWHM) (0.003 and 0.005 cm^{-1}). Additionally the spectrum of water enriched by deuterium was recorded at temperature 1370 K in the range 400-860 cm^{-1} at the resolution 0.0055 cm^{-1} with total water pressure (H_2O + HDO + D_2O) 12 torr. The measurements were done in an alumina cell with an effective length of hot gas of about 50 cm. About 1000 lines were assigned to the $D_2^{16}O$ molecule for the first time. Assignments of line transitions for medium values of rotational quantum numbers J and Ka ($12 < J$, $Ka \leq 20$) were done with the help of a calculated $D_2^{16}O$ linelist. The linelist is based on potential energy [1] and dipole moment [2] surfaces. The assignment of transitions was done using step-by-step iterative extrapolations with increasing J and Ka quantum numbers. Combination of the linelist predictions and effective rotational Hamiltonian fittings were used for this iterative procedure. The calibration of line positions was achieved using available literature data. Many new lines correspond to much higher values of rotational quantum numbers as compared to previous measurements: J_{max}= 26 and Ka_{max}= 26 for the (000) - (000) band; J_{max}= 25 and Ka_{max} = 25 for the (010) - (010) band; J_{max}= 25 and Ka_{max} = 17 for the ν_2 band. These transitions allowed us to derive an extended set of experimental rotational energy levels for (000) and (010) vibration states. We have used the RITZ code [3] to recover energy levels by simultaneous processing of our measured line positions together with other literature data. A data reduction was done by using the generation function approach for effective rotational Hamiltonian. The root mean square deviation between observed and calculated values is about 0.001 cm^{-1} for more than 2700 rotation and rotation-vibration transitions.

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HIGH-RESOLUTION ABSORPTION SPECTROSCOPY OF AN UNSTABLE SPECIES IN THE FAR-INFRARED: TENTATIVE ASSIGNMENT TO TRANS-PERP-HOONO

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Gas-phase peroxynitrous acid, HOONO (a highly unstable isomer of the well-known molecule HNO_3), has been observed very recently for the first time, produced by the gas-phase reaction between OH and NO_2 with a yield of about 5 %.[a] Therefore, this species might be an important chemical agent, in particular in the cycles of tropospheric air pollution. However, no high-resolution spectroscopy of HOONO has been reported until now, to the best of our knowledge.

During the heterogeneous synthesis of nitrous acid (HONO) we have observed a highly-structured ro-vibrational band in the far-infrared, centered around 332 cm^{-1}. The molecule leading to this spectrum was clearly produced by heterogeneous reactions since its appearence was highly dependent on the surface properties of the reaction cell. The species reached its maximum concentration in less than 3 minutes, and at total it was visible only for about 20 minutes. Nevertheless, we were able to record a well-resolved absorption spectrum using a rapid-scan Fourier-transform spectrometer (Bruker IFS 120-HR) together with a White-cell (optical path 800 cm) at a spectral resolution of 0.005 cm^{-1}. Exept for HOONO, no other known molecule of the type $H_xN_yO_z$ has a vibrational band in this region[b] and the rotational constants determined from the spacings in the *P*- and *R*-branches do not correspond to any other known nitrogen oxide or acid.

The preliminary analysis of the spectrum yields rotational constants indicating that the species might indeed be *trans-perp*-HOONO, based on a comparison with high-level *ab-initio*-calculations.[c]. Although this isomer is slightly higher in energy than the *cis-cis*-isomer of HOONO[d] it has been predicted that the production of *trans-perp*-HOONO should be favorized in gas-phase chemical reactions.[e] In additon to the first high-resolution spectrum, this study might provide the first experimental observation of gas-phase HOONO production in heterogeneous chemistry.

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THE HIGHLY RESOLVED INFRARED SPECTRUM OF CDBrClF BETWEEN 600-1300 AND 1850-2300 cm^{-1}: DETECTION OF RESONANCES, OVERTONES AND COMBINATION BANDS

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We are studying the very highly resolved rovibrational spectra ($\Delta\nu < 0.001$ cm^{-1}) of chiral molecules like CHBrClF[a], CDBrClF[b] and D1-oxirane[c]. CDBrClF, the deuterated species of CHBrClF, is one of the simplest chiral molecules. It is of fundamental interest to demonstrate molecular parity violation [d]. In order to carry out promising experiments to prove the parity violation for this molecule the highly resolved infrared spectrum has to be assigned first. We have analysed the spectrum of CDBrClF between 600 and 2300 cm^{-1} which contains the ν_6, $2\nu_8$, ν_5, ν_4, ν_3, $(\nu_6 + \nu_8)$ and $2\nu_4$ bands[e].

With our new Fourier transform infrared (FTIR) spectrometer Bruker IFS 120 HR (very high resolution prototype) we are now able to measure rovibrational spectra with a resolution up to 0.0007 cm^{-1}. Using these high resolution spectra we have detected numerous resonances, the $\nu_6/2\nu_8$ and $\nu_3/(\nu_6 + \nu_8)$ interaction pairs as well as the perturbations of the $2\nu_4$ state. These perturbations are of great interest for further carrying out Doppler-free two photon CO_2 laser transition spectroscopy. Based on these assignments we can now propose new experiments using a fast scanning submillimeter spectroscopic technique (FASSST)[f] to detect molecular parity violation for related chiral molecules in the ground state. The first Zurich FASSST spectra will be presented.

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THE ν_{19a} BAND OF FLUOROBENZENE

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The fluorobenzene molecule has been studied more as a component of van der Waals complexes, with Ar, Ne, CO, N_2 or H_2O, than as an isolated species. The large moment of inertia of the molecule induces a crowded rovibrational spectrum, and makes the analysis difficult. We present in this work an extension of the diode laser spectrum of the ν_{19a} band, corresponding to an in-plane vibration, recorded from a jet expansion at a rotational temperature of circa. 20 K, and the corresponding vibration-rotation analysis. A previous study of part of this band had been performed recently[a]. The present analysis includes new data on the R branch, which allows a more accurate determination of the rotational constants, and the first evaluation of some of the quadratic centrifugal distortion constants.

The experimental arrangement consists of a supersonic beam system crossed by the radiation of a diode laser. Liquid fluorobenzene is heated and allowed to expand with He through a valve nozzle into a vacuum chamber. The laser is a lead salt diode which emits in the 1500 cm^{-1} region. The beam is crossed several times in a multipass cell built in the vacuum chamber, and then directed to a HgCdTe infrared detector. Calibration is based on the spectrum of chloromethane and the fringes of a Ge etalon.

Even at the low temperature achieved in the expansion, the spectrum presents many coincidences which give rise to broad unresolved features. In the R region, typical groupings are formed which resemble Q sub-bands, consisting in $\Delta J = 1$ transitions with increasing values of K_a and decreasing values of J and K_c of the type (J, K_a, K_c):

$J, 0, J$; $J, 1, J$; $J-1, 1, J-2$; $J-1, 2, J-2$; $J-2, 2, J-4$; $J-2, 3, J-4$; $J-3, 3, J-6$; ...

All assigned transitions have been taken as data for the refinement of the band origin and the rotational constants of this band. Weights have been given to the data according to the estimated accuracy of each spectral region and the single or blended character of each line. All together, 445 data have been fitted with a r.m.s. of 0.0034 cm^{-1}. The rotational constants are determined with an accuracy of 60-100 kHz. Full details will be presented at the meeting.

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FIRST HIGH-RESOLUTION DETERMINATION OF THE ν_9 BAND CENTER of $^{35}ClONO_2$

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A ro-vibrational analysis of the C-type ν_8 fundamental band of $^{35}ClONO_2$ as well as the hot band, $\nu_8 + \nu_9 - \nu_9$, has been carried out using a Fourier-transform infrared spectrum of natural chlorine nitrate. This spectrum was recorded with a resolution of 0.00094 cm^{-1} at a temperature of 190 K. Accurate upper state constants have been determined for both bands including the following band centers: $\nu_0(\nu_8) = 711.20763(9)$ and $\nu_0(\nu_8 + \nu_9 - \nu_9) = 714.9050(12)$ cm^{-1}. These constants have been used, together with a transition moment operator which takes into account the observed Herman-Wallis effect, to successfully model the experimental spectrum. Moreover the constants of the 8^19^1 state have been used to model the $\nu_8 + \nu_9$ band, allowing us to assign nearly 100 Q-branch transitions and, therefore, to determine the band center of the $\nu_8 + \nu_9$ band , $\nu_0(\nu_8 + \nu_9) = 838.6269(15)$ cm^{-1}. Consequently we are able for the first time to obtain a precise band center of $\nu_9 : \nu_0(\nu_9) = 123.7219(20)$ cm^{-1}. Finally this establishes unambiguously that the band at 714.9 cm^{-1} previously attributed to $\nu_5 + \nu_7 - \nu_9$ is actually the $\nu_8 + \nu_9 - \nu_9$ hot band.

HIGH RESOLUTION RAMAN SPECTRA OF $^{12}C_2H_4$: THE ν_2 AND ν_3 FUNDAMENTALS AND THE $2\nu_{10}$ OVERTONE BAND

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The Raman spectrum of $^{12}C_2H_4$ has been recorded in the ranges 1343 - 1347 cm^{-1}, 1617 - 1626 cm^{-1}, and 1651 - 1664 cm^{-1} using an inverse Raman technique with an instrumental resolution of about 3×10^{-3} cm^{-1}. The Q branches of the ν_2 (CC stretching, A_g, at 1626.17 cm^{-1}) and ν_3 (CH_2 bending, A_g, at 1343.32 cm^{-1}) fundamental bands have been identified. The Q branch of the $2\nu_{10} \leftarrow$ G.S. transition, that is too weak to be recorded with a reasonable S/N at room temperature, has been measured at about 150 K. The origin of this band is at 1664.16 cm^{-1}.

The ν_2 and $2\nu_{10}$ bands are perturbed due to a Fermi type vibrational interaction between the $v_2 = 1$ and $v_{10} = 2$ states. The ν_3 band is also perturbed due to a Coriolis interaction between the $v_3 = 1$ and $v_6 = 1$ (B_{1g}) states.

The observed spectra of the ν_2 and $2\nu_{10}$ bands have been completely analysed assigning transitions of the sub-branches up to $K = 10$ and $J = 39$ and $K = 8$ and $J = 21$, respectively. These transitions have been fitted to a set of rovibrational parameters taking into account the Fermi interaction between the $v_2 = 1$ and the $v_{10} = 2$ states. A total of 541 out of 587 measured transitions were retained in the final cycle of the least-quares fitting procedure. Twenty-nine statistically well determined parameters , including the Fermi interaction constant and its J and K dependences, were derived giving a standard deviation of the the fit equal to 0.0007 cm^{-1}.

The analysis of the ν_3 band is more complicated since a large number of transitions appear overlapped. Nevertheless 330 transitions have been assigned with K and J values up to 9 and 25, respectively. These transitions have been fitted to a set of rovibrational parameters both ignoring or taking into account the Coriolis interaction between the $v_3 = 1$ and the $v_6 = 1$ states. The energy of the latter vibrational state has been constrained to the value reported in [a], and the rotational and distortion parameters to the corresponding ground

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HIGH RESOLUTION INFRARED AND RAMAN SPECTRA OF $^{13}C_2D_2$: ANHARMONIC RESONANCE INTERACTIONS IN THE BENDING MANIFOLD ASSOCIATED WITH ν_3

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The Q branch of the $2\nu_2 \leftarrow \nu_2$ band of $^{13}C_2D_2$ has been recorded with an instrumental resolution of about 3×10^{-3} cm^{-1} using inverse Raman spectroscopy combined with stimulated Raman pumping in order to populate the $v_2 = 1$ state. A weak local perturbation evident in the spectrum has been attributed to the effect of an anharmonic resonance between the $v_2 = 2$ and $v_3 = v_4 = v_5 = 1$ states.

To study this interaction, the components of the latter vibrational manifold (Σ_g^+, Σ_g^- and Δ_g), together with all the bending states up to $v_t = v_4 + v_5 = 2$ associated with $v_3 = 1$, have been characterised through the analysis of their infrared spectra. Both cold and hot bands from states thermally populated at room temperature, ν_4, ν_5, $2\nu_4$, $2\nu_5$, and $\nu_4 + \nu_5$, have been recorded in the region between 2300 and 3000 cm^{-1} at an effective resolution of about 0.009 cm^{-1}. A simultaneous analysis of all the assigned transitions has been performed on the basis of a theoretical model which takes into account the rotational and vibrational l-type resonances within each vibrational manifold, the Darling-Dennison anharmonic resonance between the $\nu_3 + 2\nu_4$ and $\nu_3 + 2\nu_5$ states, and the anharmonic interaction between the $2\nu_2$ and $\nu_3 + \nu_4 + \nu_5$ states.

HIGH-RESOLUTION INFRARED SPECTRA OF HCF_3 IN THE ν_6 AND $2\nu_6$ REGIONS: ROVIBRATIONAL ANALYSIS AND ACCURATE DETERMINATION OF THE GROUND STATE CONSTANTS C_0 AND D_K^0

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The high-resolution infrared spectrum of HCF_3 was studied in the ν_6 (500 cm^{-1}) and $2\nu_6$ (1000 cm^{-1}) regions. We are presenting here the results of the analysis of the ν_6 fundamental band and of the hot bands in the ν_6 region. A multiple fit analysis of the $v_6 = 1$ state, using rotational and high-resolution infrared spectra, is also presented; its results confirm the assumption that this excited state is not affected by intervibrational interactions[a]. In the $2\nu_6$ region, we report on the first observation and assignment of the $2\nu_6^{\mp 2}$ perpendicular band[b]. Using ν_6, $2\nu_6^{\pm 2} - \nu_6^{\pm 1}$ and $2\nu_6^{\mp 2}$ experimental wavenumbers, accurate C_0 and D_K^0 ground state constants were obtained, using the well-known "loop method"[c]. The results (in cm^{-1}) are the following:

$$C_0 = 0.1892550(15)$$

$$D_K^0 = 2.779(26) \times 10^{-7}$$

[a] A. Ceausu-Velcescu, J. Cosléou, J. Demaison, G. Graner, G. Duxbury, and H. Bürger, *J. Mol. Spectrosc.*, 2003 (accepted).

[b] A. Ceausu-Velcescu, H. Bürger, and G. Graner, *J. Mol. Spectrosc.*, 2003 (accepted).

[c] G. Graner and H. Bürger,in *Vibrational-Rotational Spectroscopy and Molecular Dynamics*, D. Papoušek, Ed. World Scientific, Singapore, 1998, pp. 239-297.

LINE INTENSITY MEASUREMENTS IN $^{14}N_2^{16}O$ AND THEIR TREATMENT USING THE EFFECTIVE OPERATOR APPROACH. II. THE 5200 TO 6400 cm^{-1} REGION

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This work continues a series of publications devoted to the application of the effective operators approach to the analysis and prediction of vibration-rotation spectra of linear triatomic molecules. In that frame, the present work aims at describing line intensities of cold and hot bands of $^{14}N_2^{16}O$ in its ground electronic state in the spectral range above 3600 cm^{-1}. In N_2O, vibrational interacting levels group in polyads, identified by the so-called polyad number P $= 2V_1 + V_2 + 4V_3$, as a result of the relation $2\omega_1 = 4\omega_2 = \omega_3$ existing between the harmonic frequencies. The absorption spectra of N_2O, at room temperature, have been recorded in Brussels over the whole range between 3600 and 11000 cm^{-1} using a Bruker IFS120HR Fourier transform spectrometer. The measurement and analysis of absolute line intensities in the region between 4300 and 5200 cm^{-1}, involving bands associated with transitions corresponding to $\Delta P = 7$, 8 and 9, was done recently [a]. We are now measuring absolute line intensities for cold and hot bands associated with transitions corresponding to $\Delta P = 10$ and 11, observed in the range from 5200 to 6400 cm^{-1}. Using wavefunctions previously determined from a global fit of an effective hamiltonian to about 18000 line positions [b] , parameters of a corresponding effective dipole moment are then fitted to these experimental intensities. Results will be presented and discussed.

[a] L. Daumont, J. Vander Auwera, J-L. Teffo, V. I. Perevalov and S. A. Tashkun, J. Mol. Spectrosc. 208, 281 (2001).

[b] A. Camparque,G. Weirauch, S. A. Tashkun, V. I. Perevalov, and J-L. Teffo, J. Mol. Spectrosc. 209, 198 (2001).

A NEW EXCITATION MECHANISM FOR INTERSTELLAR CLASS II METHANOL MASER TRANSITIONS BETWEEN FINE LEVELS

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Extensive surveys have shown that interstellar methanol maser emission is a widespread phenomenon, observed toward the regions of massive star formation. All methanol masers can be divided into two classes, they are distinctive. While Class I sources show enhanced absorption at frequencies of 6.7, 12.2, 107 and 157GHz, Class II sources emit prominent masers at those frequencies; while Class I methanol masers are found to be offset from HII regions, Class II methanol masers are observed toward ultracompact HII regions, and so on. The excitation mechanism of Class II masers has been a puzzle up to now.

We notice that the physical environments of maser-forming regions are various, the excitation mechanisms and conditions of these two class masers should be different from each other consequently. Therefore, we apply both the theory of laser without population inversion and the method of density matrix to argue a new mechanism. It can be used to explain the formation and behavior of each Class II methanol maser, respectively. We have verified that the $5_1 - 6_0A^+$ masers transitions at 6.7GHz and the $3_1 - 4_0A^+$ maser transitions at 107GHz can be interpreted by through the model of ladder system with coherent pumping ,2[a], and the $J_0 - J_{-1}$ E maser transitions at ~157GHz can be interpreted by through the model of V-type three-level system [c]. That implies, based on the quantum coherent effect, even there is not population inversion between upper and lower levels, there will be still net coherent light amplification – maser. Our mechanism is attractive. The bright future can be predicted.

1 H. Liu and J. Sun, Optics Comm., **150**, 152-157 (1998).
2 H. Liu and J.Sun, Chin. J. Astron.Astrophys., **2**, N.1, 51-58 (2002).
3 H. Liu, J.Sun and W.Fang, Asrtophys.& Space Science, **279**, 367-375 (2002).

Invited Lectures C

Monday, September 8, 14:00

Chairman : L. FUSINA

MASS-SELECTIVE INFRARED SPECTROSCOPY AND RELATED HIGH RESOLUTION SPECTROSCOPIC TECHNIQUES FOR INTRAMOLECULAR DYNAMICS *(45 min.)*

MICHAEL HIPPLER, *Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland*

High-resolution IR spectroscopy allows inferring information about mechanisms and time scales of fast intramolecular dynamic processes, for example intramolecular vibrational redistribution (IVR), predissociation or tunnelling processes [1]. The crucial step in extracting detailed molecular dynamics is a high-resolution analysis of complex and often weak band structures of rovibrational spectra. IR spectra are in addition often congested by hot band transitions and due to the mixture of isotopomers, which often prevents an assignment. New spectroscopic techniques which help to reduce the spectral congestion are thus very desirable. We have introduced new approaches to the IR spectroscopy of molecules in the gas phase, which are sensitive, selective and provide high spectral resolution:

In IR+UV double resonance techniques, IR spectroscopy is combined with mass spectrometry [2-4]. This allows isotopomer and mass-selective overtone spectroscopy in supersonic jet expansions, for example of chloroform, aniline and benzene isotopomers (OSVADPI, ISOS and IRSIMS [2-4]).

Cavity ring-down spectroscopy with tuneable diode lasers (cw-CRD) is a very sensitive technique for measuring absorbances, which can achieve sub-MHz resolution. In our approach, we apply cw-CRD to pulsed supersonic jet expansions [5-7], for example of $(HF)_2$ clusters.

The assignment of the jet-cooled spectra obtained by these high-resolution spectroscopic techniques gives insight into vibrational mode specific intramolecular vibrational redistribution, predissociation and tunnelling processes in the fs to ns time scales.

[1] M. Quack, Annu. Rev. Phys. Chem. 41 (1990) 839.
[2] M. Hippler and M. Quack, J. Chem. Phys. 104 (1996) 7426.
[3] B. Fehrensen, M. Hippler and M. Quack, Chem. Phys. Lett. 298 (1998) 320.
[4] M. Hippler, R. Pfab and M. Quack, submitted.
[5] M. Hippler and M. Quack, Chem. Phys. Lett. 314 (1999) 273.

[6] M. Hippler and M. Quack, J. Chem. Phys. 116 (2002) 6045.

[7] M. Hippler, L. Oeltjen and M. Quack, preliminary report in Chimia 55 (2001) 587; comprehensive paper to be published.

Molecular Physics Lecture

OVERVIEW OF CAVITY-ENHANCED ABSORPTION MEASUREMENTS *(45 min.)*

RICHARD N. ZARE, *Department of Chemistry, Stanford University, Stanford, California 94305-5080 USA*

Absorption is a nearly universal detector (except for dark matter!), but absorption often lacks sensitivity. Recently, various cavity-enhanced absorption techniques in which the sample of interest is in "optical contact" with a cavity resonator have permitted remarkable gains in sensitivity. An optical cavity (also called an optical resonator) is a region bounded by two or more mirrors that are aligned to provide multiple reflections of the radiation inside the cavity. The use of optical cavities in molecular spectroscopy has a long history dating back to the use of multi-pass cells, such as White cells, for obtaining very long effective path lengths. A significant advance has occurred with the introduction of coherent light sources, which has allowed intracavity laser absorption spectroscopy (ICLAS) to be performed. In this technique a narrow-line absorber is placed inside the cavity of a laser and the presence of the absorber strongly affects the intensity of the lasing action, particularly close to threshold. An alternative approach is to introduce a pulse of radiation in an optical cavity and measure the loss of radiant energy inside the optical cavity as a function of time, which is called the ring-down rate. From this measurement, the absorption of the sample can be determined on an absolute basis, which is essentially free from noise arising from the light source. This presentation will primarily emphasize cavity ring-down spectroscopy (CRDS) and related techniques. Following a brief review of the principles of CRDS, attention will be placed on how to make such measurements quantitative. The talk will conclude by describing recent work in the author's laboratory using CRDS and its variants to detect trace species in liquids and at interfaces and to determine the time-dependent concentrations of these species.

Poster Session D

Monday, September 8, 16:00

WEAK OVERTONE TRANSITIONS OF N_2O AROUND 1.05 μm BY ICLAS-VECSEL

Y. DING, E. BERTSEVA AND A. CAMPARGUE, *Laboratoire de Spectrométrie Physique (associated with CNRS UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint Martin d'Hères, France*; **V. I. PEREVALOV, S. A. TASHKUN**, *Institute of Atmospheric Optics, SB, Russian Academy of Sciences, 634055, Tomsk, Russia*; **J. -L. TEFFO**, *Laboratoire de Physique Moléculaire et Applications, C.N.R.S.(Laboratoire associé l' Université Pierre et Marie Curie), Case 76, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France*; **S. HU**, *Laboratory of Bond-Selective Chemistry, University of Science and Technology of China, Hefei, 230026, People's Republic of China*

The weak overtone transitions of nitrous oxide, N_2O, have been investigated around 1.05 μm by Fourier Transform spectroscopy and Intracavity Laser Absorption Spectroscopy (ICLAS) using different Vertical External Cavity Surface Emitting Lasers (VECSEL). Nine bands were rotationally analyzed revealing the occurrence of some local rotational perturbations. The interaction mechanisms and the perturbers are univocally assigned on the basis of the effective Hamiltonian model. In two cases, interpolyad couplings were evidenced indicating that the polyad version of the effective Hamiltonian has to be extended to include Coriolis and interpolyad anharmonic interactions. The preliminary results of the global fitting of the line positions of this molecule using nonpolyad model of effective Hamiltonian will be also presented.

INCOHERENT BROAD-BAND CAVITY ENHANCED ABSORPTION SPECTROSCOPY

ALBERT A. RUTH, *Department of Physics, National University of Ireland, University College Cork, Cork, Ireland*; **SVEN E. FIEDLER**, **ACHIM HESE**, *Institut für Atomare Physik und Fachdidaktik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany*

A new very sensitive method for incoherent broad-band cavity enhanced absorption measurements of gaseous samples, using a white-light source is demonstrated. The light of a short-arc Xe-lamp transmitted by an optically stable cavity is dispersed with a grating monochromator and detected by a sensitive photodiode-array. The technique is a development of the previously published principle of cavity enhanced absorption spectroscopy [R. Engeln et al., Rev. Sci. Instr. 69 (1998) 3763]. The method is characterized by great experimental simplicity, high sensitivity, and high temporal resolution. The poster will outline these features on basis of a measurement of the $b^1\Sigma_g^+(\nu' = 2) \leftarrow X^3\Sigma_g^-(\nu'' = 0)$ absorption transition of molecular oxygen and the $S_{1,n} \leftarrow S_0$ absorption spectrum of gaseous azulene at its vapour pressure at room temperature as well as in a supersonic jet.

CAVITY RINGDOWN ABSORPTION SPECTRUM AND RING-BENDING POTENTIAL ENERGY FUNCTION OF THE $T_1(n,\pi^*)$ STATE OF 2-CYCLOPENTEN-1-ONE

NATHAN R. PILLSBURY, STEPHEN DRUCKER, *Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702*; **JAEBUM CHOO**, *Department of Chemistry, Hanyang University, Ansan 425-791, Korea*; **JAAN LAANE**, *Department of Chemistry, Texas A & M University, College Station, TX 77843*

The room-temperature cavity ringdown absorption spectra of 2-cyclopenten-1-one (2CP) and deuterated derivatives were recorded near 385 nm. The very weak ($\epsilon < 1\ M^{-1}\ cm^{-1}$) band system in this region is assigned to the $T_1(n,\pi^*) \leftarrow S_0$ electronic transition. The origin band was observed at 25,963.6 cm^{-1} for the undeuterated molecule and at 25,959.4 and 25,956.2 cm^{-1}, respectively, for 2CP-5-d_1 and 2CP-5,5-d_2. For the $-d_0$ isotopomer, about 50 vibronic transitions have been assigned in a region from -500 to $+500$ cm^{-1} relative to the origin band. Several excited-state fundamentals have been determined for the d_0/d_2 isotopomers, including ring-twisting (ν'_{29}), out-of-plane carbonyl deformation (ν'_{28}), and in-plane carbonyl deformation (ν'_{19}). Nearly every corresponding assignment was made in the $-d_2$ spectrum. The five lowest ring-bending (ν'_{30}) energy levels for the T_1 state were also determined. The spectroscopic results are summarized below (frequencies in cm^{-1}):

mode	d_0	d_2	v'_{30}	d_0	d_2
ν'_{29}	238.9	227.8	1	36.5	29.7
ν'_{28}	346.3	330.2	2	118.9	101.9
ν'_{19}	431.8	420.3	3	213.7	184.8
			4	324.5	280.5
			5	446.4	385.6

A potential-energy function of the form ax^4+bx^2 was fit to the ring-bending levels for each isotopic species. The fitting procedure utilized a kinetic-energy expansion that was calculated based on the structure obtained for the $T_1(n,\pi^*)$ state from density functional calculations. The barrier to planarity, determined from the best-fitting potential energy functions for the $-d_0$, $-d_1$, and $-d_2$ species, ranges from 42.0 to 43.5 cm^{-1}. In the T_1 state, electron repulsion resulting from the spin flip favors nonplanarity. The S_0 and $S_1(n,\pi^*)$ states have planar structures that are stabilized by conjugation.

A COMPARISON OF WAVELENGTH MODULATION AND CAVITY ENHANCED ABSORPTION SPECTROSCOPY FOR TRACE MOLECULE DETECTION IN THE NIR

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We have developed a near infrared (NIR) tuneable diode laser spectrometer for tropospheric trace molecule detection. The spectrometer is based upon an extended cavity grating tuned diode laser, which can operate in the region from 1.8 to 1.3 μm. The output beam then passed through long absorption path length an on to a room temperature semiconductor detector. The diode laser and the data acquisition and gas flow systems of the instrument are controlled using LabView. The spectrometer has been designed so that a simultaneous comparison can be made between the performance of a Herriot absorption cell using wavelength modulation spectroscopy and a high finesse cavity used for cavity enhanced absorption spectroscopy. We will show examples of spectra of ammonia and other gases recorded in this way and discuss the relative merits of these two methods.

Field trials of a breadboard version of this instrument have been carried out to compare its performance with a mid infrared lead salt laser spectrometer, using an astigmatic absorption cell, developed by D.J. Brassington's group at the Imperial College ACRU unit at Ascot. The measurements will be real-time sampling from the environment at Silwood Park, through an inlet system. One of the principal molecules for this comparison will be formaldehyde.

ROTATIONALLY RESOLVED OVERTONE COMBINATION BANDS OF FORMALDEHYDE AT 1.5 μm INVESTIGATED BY CAVITY ENHANCED ABSORPTION SPECTROSCOPY

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Diode-laser based cavity enhanced absorption spectroscopy (CEAS) is used to investigate the absorption of ground state formaldehyde (H_2CO) between ~6610 and 6710 cm^{-1}. In this region six weak combination overtones of formaldehyde are located [1], of which $3\nu_2+\nu_3$ (6652 cm^{-1}, a_1) and $\nu_2+\nu_3+3\nu_4$ (6693 cm^{-1}, b_1) are the most prominent. Rotational lines of the combination bands were measured at room temperature with a spectral resolution of ~70 MHz. Typical line-widths (FWHM) are of the order of 600 MHz at a pressure of 8 mbar. Absolute absorption coefficients are estimated and spectral positions were calibrated using known ammonia overtones in the same spectral region.

[1] R.J. Bouwens, J.A. Hammerschmidt, M.M. Grzeskowiak, T.A. Stegink, P.M. Yorba and W.F. Polik; *J. Chem. Phys.*, 104 (1996) 460.

CAVITY-ENHANCED BROAD-BAND ABSORPTION SPECTROSCOPY WITH A FEMTOSECOND LASER: APPLICATION TO THE OVERTONE SPECTROSCOPY OF ACETYLENE IN THE BLUE

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Light resonating inside an optical cavity interacts with the intracavity medium over a number of passes proportional to the cavity finesse F. Interference over multiple passes gives a transmission spectrum as a comb of peaks, spaced by the Free Spectral Range of the cavity, $FSR = c/2L$, where L is the cavity length. Intracavity sample absorption at the frequency of a mode will reduce its integrated transmission as if the effective path length was $F \cdot L/\pi$. This is the principle of cavity enhanced absorption spectroscopy.

Modelocked lasers feature an emission spectrum composed of a comb of narrow peaks with a broad and smooth envelope, which is an ideal background for absorption spectroscopy. We have recently performed the injection of whole spectrum of a femtosecond Ti:Sa laser into an optical cavity by tuning the cavity length to the 'magic point', where its FSR becomes coincides to the modelocked laser comb. Cavity enhanced absorption lines were then observed over the about 5 nm broad envelope of the laser by a spectrograph equipped with a CCD array [a].

Frequency doubling of the Ti:Sa laser gives access to the blue region which is not accessible by ICLAS. As an illustration of the capabilities of this technique, the high overtone band of C_2H_2 was recorded near 23813 cm^{-1} ($\sim$ 420 nm). The results of the rovibrational analysis of this transition which corresponds to $\Delta\nu_{CH} = 8$ stretching excitation will be presented and discussed.

[a] T. Gherman and D. Romanini, *Optics Express*, **10**, 1033 (2002)

FIRST STUDY OF JET-COOLED BIS(BENZENE)CHROMIUM BY HIGH-RESOLUTION REMPI AND ZEKE-MATI SPECTROSCOPY

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Two-colour resonance-enhanced multiphoton ionisation (REMPI) and zero kinetic energy mass-analysed threshold ionisation (ZEKE-MATI) spectra of one of the most important sandwich organometallics, $(\eta^6\text{-}C_6H_6)_2Cr$, have been obtained for the first time with use of the $3d_z2 \rightarrow R4p_{x,y}$ Rydberg transition as the initial step of the electronic excitation. The first ionisation potential of $(\eta^6\text{-}C_6H_6)_2Cr$ determined on the basis of the high-resolution ZEKE-MATI spectrum is 44087 $\pm$ 3 cm^{-1}, which agrees very well with that found from the frequencies of the higher Rydberg series members [a] (44090 cm^{-1}). The binding energy of the $R4p_{x,y}$ electron is 17333 $\pm$ 5 cm^{-1}. The REMPI spectrum shows vibronic components separated by 263 and 790 cm^{-1} from the 0,0 peak. These values correspond to the frequencies of the symmetric metal-ring stretching vibration ν_{21} and CH umbrella vibration ν_{11as}, respectively, of the free bis(η^6-benzene)chromium neutral molecule in the Rydberg state. The excitation of $(\eta^6\text{-}C_6H_6)_2Cr$ through the vibronic components of the $3d_z2 \rightarrow R4p_{x,y}$ transition produces ZEKE-MATI signals corresponding to the vibrational levels of the molecular cation. The ν_{21} and ν_{11as} vibrational frequencies of gas-phase $(\eta^6\text{-}C_6H_6)_2Cr^+$ (262 $\pm$ 5 and 788 $\pm$ 4 cm^{-1}, respectively) have been found from these ZEKE-MATI spectra. The ν_{21} and ν_{11as} frequencies determined in this work are close to those found from the Raman spectrum of solid-state bis(η^6-benzene)chromium [b] (277 and 791 cm^{-1}, respectively) and from the DFT calculations [c] (259.4 and 762.1 cm^{-1}, respectively).

This research was supported by the Alexander von Humboldt Foundation, the Russian Foundation for Basic Research (Project N 03-03-32944), the Science Support Foundation and the DFG (SFB 377)

1. U. Even, R. D. Levine and R. Bersohn, *J. Phys. Chem.*, **98**, 3472-3477 (1994).
2. S. J. Cyvin, J. Brunvoll and L. Schäfer, *J. Chem. Phys.*, **54**, 1517-1522 (1971).
3. A. Bérces and T. Ziegler, *J. Phys. Chem.*, **98**, 13233-13242 (1994).

TWO-COLOR REMPI SPECTROSCOPY OF JET-COOLED FERROCENE AND NICKELOCENE

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The wavelength-dependent mass-selected ion signals produced by supersonic-cooled ferrocene and nickelocene irradiated with nanosecond laser pulses in the region of the first Rydberg p transition (40000 - 42000 and 34500-36000 cm^{-1}, respectively) have been investigated. Surprisingly, in a one-color multiphoton experiment conditions have been found for formation of intact molecular ions $(C_5H_5)_2M^+$ (M = Fe, Ni) as the only ionic product. The yield of molecular ions increases significantly in a two-color experiment when the second laser operates in the 17500 cm^{-1}. The two-color REMPI excitation spectrum of ferrocene measured at the masses of $(C_5H_5)_2Fe^+$ shows a 0_0^0 peak at 41090 cm^{-1} and a 4_0^1 component at 41410 cm^{-1} demonstrating better resolution than the one-photon absorption spectrum measured in a static cell at elevated temperature [a]. The distance between the vibronic components corresponds to the symmetric metal-ligand stretch in the Rydberg state. Similar vibronic components have been found in the multiphoton dissociation/multiphoton ionization spectrum of jet-cooled ferrocene measured at masses of Fe^+ with the second laser frequency corresponding to a resonance line of Fe(I). No vibronic structure is observed in the REMPI spectrum of nickelocene. This is due to the antibonding character of the nickelocene HOMO ionized. The two-color $(C_5H_5)_2Ni^+$ signal dependence on the frequency of the second laser gives an upper limit for the adiabatic first ionization potential of nickelocene as 6.138 ± 0.012 eV.

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1. S. Y. Ketkov and G. A. Domrachev, *J. Organomet. Chem.*, **420**, 67-77 (1991).

CALCULATING THE ENERGY LEVELS OF ISOMERIZING TETRAATOMIC MOLECULES: THE ROVIBRATIONAL STATES OF Ar_2HF

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We have developed a general, six-dimensional computational method for the accurate calculation of rotationally and vibrationally excited states of tetra-atomic molecules. The resulting computer program [a] is particularly appropriate for molecules executing wide-amplitude motions and isomerizations. An application to the Ar_2HF van der Waals trimer is presented, in which the HF intramolecular stretching coordinate is separated out adiabatically and is not treated explicitly. Vibrational term values up to about 100 cm^{-1}, with absolute convergence to better than 0.1 cm^{-1}, are reported. These calculations employ more extensive vibrational basis sets and hence consider a much higher density of states than hitherto. States that sample Ar–Ar–HF linear configurations and approach Ar–HF–Ar linear configurations are characterized for the first time.

Ar_2HF is an important prototype system for studying non-additive intermolecular forces, because the Ar–Ar and Ar–HF potentials are well known and the experimental vibrational frequencies are significantly different from those predicted on the basis of pairwise additivity. In previous work, the differences in vibrational frequencies have been used to develop and test models of non-additive intermolecular forces [b]. However, up to now, the methods available for calculating rotational constants from potential surfaces neglected Coriolis effects and were not accurate enough to allow the experimental rotational constants to be used for the same purpose. In the present work, we are able to use calculations for total angular momentum $J = 0$ and 1 to provide the first accurate calculations of rotational constants for this system. The rotational constants for the HF bending states of Ar_2HF in the ground and first vibrationally excited states of the HF monomer are in much improved agreement with experiment. In future work, we hope to improve the convergence enough

[a] I. N. Kozin, M. M. Law, J. M. Hutson and J. Tennyson, *J. Chem. Phys.* **118**, 4896 (2003).

[b] A. Ernesti and J. M. Hutson, *J. Chem. Phys.* **106**, 6288 (1997).

to use the trimer rotational constants to provide further tests of models of non-additive forces.

One of the experimentally important states is the in-plane HF bend, about 60 cm^{-1} above the ground state. Because of the importance of linear configurations, the density of states involving heavy-atom framework vibrations at this energy is greater than in earlier calculations[b], and one of them mixes strongly with the in-plane bend. Both the combinations have substantial calculated intensity. This may explain why only about 60% of the resolved lines in the infrared spectrum could be assigned[c].

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ARE THE SPLITTINGS IN THE ν_6 FUNDAMENTAL OF 1-CHLORO-1,1-DIFLUOROETHANE (HCFC-142b) CAUSED BY INTERACTION WITH AN HIGHLY EXCITED TORSIONAL LEVEL?

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High resolution infrared spectra (0.0012 cm^{-1} FWHM) have been measured for mixtures of 1-chloro-1,1-difluoroethane in Ne, expanded in a supersonic planar jet. The ν_6 fundamental, being a C-C stretching mode, appears as a strong A-type band around 1135.4 cm^{-1}, and shows a prominent unresolved Q-branch, and P and R-branch clusters with well resolved clusters up to J=25. The isotopic ^{35}Cl-^{37}Cl shift is rather large (1.8 cm^{-1}) and the transitions due to the $CH_3CF_2{}^{37}Cl$ isotopomer are generally well resolved and easily distinguishable from the more abundant $CH_3CF_2{}^{35}Cl$ molecule. For both isotopomers we observe a large splitting (about 0.03-0.04 cm^{-1}) throughout the spectrum. For low K_a values each rotational transition is splitted in two components of about the same intensity, for higher K_a there seems to be a further splitting of one of the two components. Our hypothesis is that a Fermi resonance occurs between ν_6 and a nearby vibrational level, containing three or more torsional quanta (the torsion fundamental is predicted at about 270 cm^{-1}). This combination level is supposed to split in A and E levels, due to the threefold torsional potential. Although this A-E splitting is small in the ground state ($\ll$ 1 MHz, as calculated from a V_3= 1312 cm^{-1}) it becomes appreciable for highly excited torsional states ($\approx$ 0.12 cm^{-1} for $n_{tors} = 3$ and $\approx$ 1.5 cm^{-1} for $n_{tors} = 4$).

CALCULATION OF SPECTROSCOPIC CONSTANTS AND EFFECTIVE ROVIBRATIONAL PARAMETERS FOR TRIATOMIC C_{2v} AND C_s ISOTOPOMERS FROM POTENTIAL ENERGY FUNCTIONS

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Accurate empirically determined and/or ab initio potential energy surfaces (PES) for the electronic ground state have been recently determined for several triatomic molecules (see for example [1-4] and references therein). On the other hand analysis of experimental high-resolution spectra require reliable estimations for various spectroscopic constants, including force and centrifugal distortion constants as well as Coriolis, Fermi, Darlig-Dennison and other resonance coupling parameters etc. The latter information is missing for many highly excited states and polyads in particular for isotopic species.

The aim of the present work is to develop a software package allowing to make systematic calculations of effective Hamiltonian and transition moment parameters from any analytically defined potential and dipole moment surfaces. This suite of routines contains various codes of formal and numerical calculations for

- PES and DMS surfaces analyses, coordinate and axes transformations,
- full rovibrational Hamiltonian expansion in normal coordinates for C_{2v} and C_s species,
- change of various operator representations and orderings,
- high-order rovibrational (anti)commutator calculations,
- transformation to effective Hamiltonians for given resonance conditions,
- effective Hamiltonian reductions.

An essential part is the code of formal Contact Transformation allowing to construct effective ro-vibrational Hamiltonians for successive polyads starting with a PES for nuclear motion in a given electronic state discussed at the separate poster [5]. Some applications to C_{2v} and C_s isotopomers of asymmetric-top triatomic molecules with examples using recent accurate PES

will be discussed.

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COMPUTER IMPLEMENTATION OF CONTACT TRANSFORMATIONS FOR ROVIBRATIONAL HAMILTONIANS : MOL_CT CODE OF FORMAL CALCULATIONS

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Applications of effective Hamiltonian models and of global variational calculations using potential energy surfaces (PES) have shown specific advantages and problems and proved to be complementary for high-resolution spectra analysis: see for example a comparative discussion[1] of these approaches for spectroscopic databases calculations. "Local" effective models have been most widely used in high-resolution spectroscopy because this allows achieving a good accuracy for low and medium quantum numbers using relatively simple computations. These models are usually derived by applying Contact Transformations (CT)[2–4], or alternative forms of the perturbation theory to simplify a full rovibrational Hamiltonian. This provides a mathematical background for intuitively introduced physical models for bound states of semi-rigid molecules near the equilibrium configuration and gives a simple interpretation of effective parameters. However apart from the case of diatomic molecules, where analytical computer assisted CT have been carried out to 20-th order of perturbation theory[5], only lower relations for effective spectroscopic are available in the literature.

This project is aimed at building systematic links between global variational and effective Hamiltonian approaches via the specialized package MOL_CT designed to perform ro-vibrational algebra computations for polyatomic molecules in a mixed numerical/analytical form. The computer implementation of the general algorithm[4] of high-order CT calculations as well as convergence and ordering issues are discussed. The code allows a systematic computer assisted construction of effective ro-vibrational Hamiltonians for successive polyads starting with a PES for nuclear motion in a given electronic state. Some applications to asymmetric-top triatomic molecules will be

discussed.

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CALCULATING THE ENERGY LEVELS OF ISOMERIZING TETRAATOMIC MOLECULES: THE WAVR4 CODE AND APPLICATION TO THE VIBRATIONAL STATES OF ACETYLENE/VINYLIDENE

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We have developed a general, six-dimensional computational method for the accurate calculation of rotationally and vibrationally excited states of tetra-atomic molecules. The resulting computer program, WAVR4[a] is particularly appropriate for molecules and complexes executing wide-amplitude motions and isomerizations.

The solution strategy for the vibrational problem uses a discrete variable representation (DVR) for the radial coordinates and a basis representation (FBR) for the angular coordinates. A range of coordinate systems are available based on orthogonal internal vectors: Jacobi, Radau, diatom + diatom and (orthogonalised) satellite vectors. A sequential diagonalisation-truncation scheme is employed. First, the 3D angular basis is contracted at each radial point. Then one (or two) of the radial coordinates is included to give a contracted 4D (or 5D) basis. Finally the remaining radial coordinate(s) are included and the full 6D Hamiltonian matrix diagonalised. After each intermediate diagonalisation only states below a certain energy cut-off are retained for use in the subsequent stages.

Morse-oscillator-like and spherical oscillator functions are available to describe the radial basis functions. The angular basis is constructed using coupled spherical harmonics and Legendre functions. Terms in the kinetic energy operator involving $1/R^2$ terms may be handled analytically or using the quadrature approximation.

For rotationally excited, $J > 0$ calculations we have employed a two step procedure: first the Hamiltonian matrix is diagonalised for K diagonal and then these solutions used as a basis for the full $J > 0$ calculation.

An application to the Ar_2HF van der Waals trimer is presented in an accompanying poster. Here we present the application to the acetylene/vinylidene

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isomerising system. Initial calculations have been performed for acetylene using a new accurate potential developed by Zou and Bowman[b]. Vibrational energy levels have been computed using diatom-diatom (HC–CH) and orthogonal satellite (H–CC–H) coordinate systems. There is a good agreement between the two. Comparisons are also made with energy levels computed[b] using the other possible diatom-diatom scheme (HH—CC). The Zou and Bowman potential is suitable for studying the acetylene/vinylidene isomerisation and we are attempting to extend our calculations to higher energies to study vinylidene states. This work is being pursued using a newly developed parallelised version of the WAVR4 code.

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THE N=2 CH-CHROMOPHORE ABSORPTION NEAR 6000 CM^{-1} OF BENZENE ISOTOPOMERS BY MASS-SELECTIVE OVERTONE SPECTROSCOPY WITH IR+UV IONISATION DETECTION

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The detailed analysis of overtone spectra allows the study of intramolecular dynamics of molecules in highly vibrationally excited states, e.g. to extract mechanisms and time scales of intramolecular vibrational redistribution (IVR) processes [1]. Overtone spectra of benzene are difficult to analyse, however: Spectra at room temperature are heavily congested by hot-band transitions, and the homogeneous structure due to intramolecular vibrational redistribution is rather complex. In addition, there are several C-isotopomers of benzene present at natural abundance, which can not be separated by conventional spectroscopic techniques. Employing our recently introduced IR+UV double-resonance scheme for obtaining mass-resolved infrared spectra [2-4], the isotopomer selected N=2 CH-chromophore absorption of $^{12}C_6H_6$ and $^{13}C^{12}C_5H_6$ near 6000 cm^{-1} has been recorded in a supersonic jet expansion of the benzene isotopomer mixture at natural abundance [4].

The $^{13}C^{12}C_5H_6$ spectra are the first of this kind reported in the literature. The $^{12}C_6H_6$ spectrum is compatible with a proposed model of intramolecular vibrational redistribution with a distinct hierarchy of time scales: the CH-stretching state is the IR chromophore state coupled to the IR field. With a decay time of 100 fs, vibrational excitation is redistributed to a first tier of vibrational states, probably CH-stretching/bending combination bands coupled by strong Fermi resonances. Vibrational excitation is then further redistributed with 0.35 ps to a second tier of states, possibly by weaker higher order anharmonic resonances. The observed line widths give a lower bound for the decay time into the dense background manifold, 1.3 ps. Although the experimental jet spectra are in qualitative agreement with previously published calculated spectra, they clearly disagree in finer details.

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MULTIPHOTON ABSORPTION SPECTROSCOPY: REMPI-TOF ANALYSIS OF HCl AND DCl

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(2+1) and (3+1) resonance enhanced multiphoton ionization (REMPI) spectra of selected isotopomers of HCl and DCl were recorded and analysed. Simulation analysis of (3+1)REMPI spectra, based on transition probabilities for three-photon absorption, reveal "new" electronic states, $^3\Phi_3$, not observed in single- and two-photon absorption. The analyses allowed determination of rotational and vibrational spectroscopic parameters for the excited states. Furthermore, (3+1)REMPI spectra of HCl and DCl, involving three-photon transitions to the $j(^3\Sigma^-(0^+))$ state, are also recorded and analysed for the first time. Clear evidence for near resonance interactions between the j and the $V(^1\Sigma^+)$ ion-pair state is seen both in the (3+1) and (2+1)REMPI spectra of HCl. The interaction strength is evaluated by model calculations, based on perturbation theory and deperturbed energy levels [a] [b] [c].

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RYDBERG-STATE-RESOLVED THRESHOLD-IONIZATION SPECTROSCOPY: APPLICATION TO CO^+ AND NH_3^+

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We have recently developed a method called Rydberg-state-resolved threshold-ionization (RSR-TI) spectroscopy that enables the determination of high-resolution spectroscopic information on molecular cations by photoelectron spectroscopy.
It consists of resolving the individual high n Rydberg states (principal quantum number $n > 150$) which are normally detected as an unresolved broad feature in pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. The precision in the determination of the ionization thresholds is only limited by the bandwidth of the radiation source used for photoexcitation (250 MHz in the case of our near-Fourier-transform-limited VUV laser). The method is also used to measure the separation of very close lying ionic energy levels by observing the "beat"-pattern that appears when two Rydberg series converge at these two thresholds.
We demonstrate the power of this method by applying it to the cations of CO and NH_3 and determining their first adiabatic ionization thresholds and spin-rotation splittings with an unprecedented accuracy.

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MOLECULAR ASSOCIATION IN METHANOL AND ETHANOL

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The Raman spectra of methanol and ethanol were studied in wide temperature range at different rates of temperature changings. The quantum mechanical calculations of parameters of vibrational spectra of free molecule and some associates were made The quantum mechanical calculations of the formation energy and the optimal space configurations of the molecular associations of methanol molecules, which consist of two, three and four molecules were made too. The spectra were calculated in harmonic approximation. Comparison of these results and experimental data allows to insist that there are no monomers and dimers in liquid methanol. The only stable forms are cyclic clusters. The widths of the bands do not depend on temperature and this fact indicates the stability of methanol structure in condenced state.

INTRAMOLECULAR HYDROGEN BOND DYNAMICS IN X-CH_2-CH_2-X, X=CH_3, NH_2, PH_2, OH, SH

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While studying the donor-acceptor interchange tunnelling of ethylene diamine by microwave spectroscopy and ab initio methods we became also interested in the hydrogen bond dynamics of similar compounds. Microwave data are available for butane [1], H_3C-CH_2-CH_2-CH_3, ethylene diamine [2], H_2N-CH_2-CH_2-NH_2, ethylene diphosphine [3], H_2P-CH_2-CH_2-PH_2, glycole [4,5,6], HO-CH_2-CH_2-OH, and thioglycole [7], HS-CH_2-CH_2-SH.

In this work we will focus on ab initio calculations and on the interpretation of the theoretical data in terms of parameters which can be directly compared to experimental data. Using the same quantum chemical methods and basis sets we calculated two-dimensional energy surfaces for all compounds. While both substituents X were rotated in several steps around the C-X axes, all other structural parameters were allowed to relax. The energy surfaces obtained this way were parametrized by symmetry adapted two-dimensional Fourier expansions. Using a simple model with two planar rotors hindered by the torsional potential obtained above, we set up the Hamiltonian matrix in a symmetry adapted free rotor basis and diagonalized it in order to obtain the torsional wave functions and energy eigenvalues. This allowed us to predict tunneling splittings and to compare them with experimental finding.

The situation of the hydrogen bonds in the compounds studied is quite different. The energy surface of butane is very symmetric and there is no evidence for hydrogen bonds at all. Ethylene diamine has at least two different strongly hydrogen bonded conformers whereas the ability of ethylene diphosphine to form hydrogen bonds is much weaker. A similar situation was found for glycole and thioglycole, were the influence of intermolecular hydrogen bonds is much stronger in glycole than in thioglycole.

The agreement between experimental and theoretical results was found to be quite satisfactory in most cases, but also discrepancies were found. E.g. the tunneling splitting predicted for conformer I of ethylene diamine turned out to be in reasonable agreement with the experimental result, but the experimental splitting of conformer II is orders of magnitude bigger than our prediction. This disagreement may be attributed to our very simple model

which presently does not include inversional motions of the amino groups.

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NEGATIVE ION MOTION IN THE MIXTURES OF SF_6 WITH CF_4 and CH_4-ARGON

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This paper deals with the measurement of the mobility of negative ions in the mixtures of SF_6 with CF_4, and the CH_4-Ar (50:50) binary mixture, with SF_6 contents of up to 50 %. The Pulsed Townsend Technique was used to produce the ionic avalanches from two distinct approaches, over the low E/N range in which ionization is either negligible or absent, and attachment processes are significant. The E/N range of measurement was 1 to 100 Td. The structure of the measured signals strongly suggests that there is only one negative ion, most likely formed by resonant attachment. A test of the measured mobilities with Blanc.s law provides further support to ascribe the drifting species to SF_6^-.

MOLECULAR MATTER WAVE INTERFEROMETRY: TOOL FOR STUDYING WEAK INFLUENCES ON MOLECULES AND HIGH PRECISION MOLECULAR BEAM SPECTROSCOPY?

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A molecular Ramsey-Bordé Matter Wave Interferometer [1] is applied to study weak influences on the molecular matter wave, like collisions at low energies or weak external fields. The interferometer operates with K_2 molecules in a beam, which is composed of K- atoms and few percent molecules.Both particles have similar velocities, so that the collisions between atoms and molecules have low collisional energies and can be adressed as being "cold". The interference pattern will change in amplitude and phase due to the weak interaction. These effects are very small. For an effect modulation we reduce the number of atoms in the beam by deflection or change the electronic state of the atoms periodically. The interferometer uses levels of the triplet manifold $b\,^3\Pi_u$. For these states an inversion analysis was published recently [2], with which the degree of admixture and the lifetime can be calculated. The interferometer will also be used to study the influence of weak external fields on the molecular matter wave. The present state of the experiment will be reported.

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INELASTIC SPUTTERING OF IONIC CRYSTALS UNDER ELECTRON AND MULTICHARGED ION BOMBARDMENT

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Using the method of secondary ion mass-spectrometry the yield of positive ions from LiF, KCl, KBr has been investigated during the bombardment by electrons and Ar ions with the charge $q = 1-6$ with in the range of energy $E = 0.02 - 1$ KeV. It has been shown that the increase in q and E of bombarding ions gives the rise in the yield of Li^+, K^+, F^+, Cl^+, Br^+ and slightly affects the yield of molecular ions $(M_nX_n)^+$.

Inelastic sputtering has its hold on charge and occurs at $q > 2$. Potential energy of MCI is spent on the formation of neutrals X and double - ionized anions X^+. Double - ionized ions M_2^+ have not been found in the mass-spectra for all the initial values of the charge q. During the electron bombardment of alkali-halide crystals the multiple -charged ions M_2^+, X_2^+, M_3^+, X_3^+ have been found together with atomic and molecular ions. Their occurrence is connected with the Auger effect as a result of excitation of inner shells of cations and anions.

The rise of the MCI share results in the yield of one-charged ions. From the comparison of ion emission taking place under the action of the both beams, it has been concluded that ionization of the lattice atoms by electrons is more effective than by ions.

A METHOD OF CALCULATING ANHARMONIC VIBRATIONAL SPECTRA OF MOLECULES

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A method based on solving an integral Schrödinger equation for nonlinear multidimensional oscillator has been suggested. For the case of one–dimensional nonlinear oscillator one may write down the following integral equation

$$\psi\,(Q) \;=\; \int_{-\infty}^{\infty} dQ' \left(E - \lambda\,\hat{V}_{anh}\,(Q')\right)\; G\,(Q,Q')\;\psi\;(Q') \qquad (1)$$

with $G\,(Q,Q') \;=\; \int_{0}^{\infty} \rho_0\;(Q,Q';\beta)\;d\beta$, and $\rho_0\;(Q,Q';\beta)$ being a density of a harmonic oscillator

$$\rho_0\;(Q,Q';\beta) \;=\; \sum_{v} e^{-\beta\,\varepsilon_v} \varphi_v\,(Q)\;\varphi_v\,(Q') \;\;;$$

$\hat{V}_{anh}\,(Q')$ is an anharmonic part of the vibrational potential. Using a method of successive iteration of the Eq. (1) we obtain successive approximation for anharmonic wave function.

For polyatomic molecules this method allows to get rid of computational difficulties coming from Fermi resonances.

ABSOLUTE LINE INTENSITIES FOR CARBONYL SULFIDE NEAR 4.85μm

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This work involves measurements of individual absorption line intensities for bands of carbonyl sulfide observed in the region between 600 and 3300 cm^{-1}. Initially, the very strong ν_3 band near 2062 cm^{-1} and bands closeby were our targets. We eventually extended the measurements to bands observed in the wider range mentioned above, from ν_1 near 859 cm^{-1} to $\nu_1 + \nu_3$ near 2916 cm^{-1}, in an attempt to assess the agreement with previous work.

Absorption spectra of carbonyl sulfide were recorded using a Bruker IFS 120HR Fourier transform spectrometer, at resolutions of 0.002 cm^{-1} for the spectral region below 1900 cm^{-1} and 0.003 cm^{-1} for the range above (Maximum Optical Path Difference = 450 and 300 cm respectively). Carbonyl sulfide (Aldrich, 96+% purity) was purified by pumping the sample kept at −78 C with a methanol / dry ice bath until the volume had reduced to about a quarter its initial size. We checked that only negligible amounts of the main impurities (CO, CO_2 and CS_2) remained in the purified sample. The spectra of carbonyl sulfide were recorded at 296 K, using two thermostatised absorption cells, 1.43 and 20 cm long, and sample pressures ranging from 0.098 to 100 mbar.

We measured line intensities as described in previous contributions,[a] modeling the molecular line shape with a Gaussian or Voigt profile and freezing the pressure self-broadening parameter involved in the latter to values from HITRAN 2000.[b] Eventually, it appeared necessary to determine pressure self-broadening coefficients for lines with $|m| > 55$. Transition dipole moments are derived from the line intensities, using eigenvectors from global analysis[c] to describe the Herman-Wallis dependences observed. This work is in progress. Current results will be presented and compared with previous work.

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HIGH RESOLULTION SPECTROSCOPIC STUDIES OF VIBRATIONAL STATES IN THE TRIPLET POTENTIAL SURFACES OF ACETYLENE

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Since acetylene in the lowest triplet state (T_1) was predicted that there are three local minima at *cis* -, *trans* -, and vinylidene configurations by theoretical calculations, an isomerization reaction among those configurations has been paid a lot of attentions. We have observed an electronic transition between the T_2 - T_1 potential energy surface at the *cis* - configuration around 7400 cm^{-1} region by using high resolution near-IR diode laser kinetic spectroscopy combined with a pulsed mercury photo-sensitized reaction.

$$Hg^*(^3P) + HCCH(X\,^1\Sigma) \longrightarrow Hg(^1S) + HCCH(a\,^3B_2)$$

By now 0-0 band of C_2H_2, C_2HD and C_2D_2 have been observed in Doppler limited resolution and rotational analysis have been performed. However, vibrational excitation in the bending modes is essentially important for the *cis -trans* isomerization. It is very promising to detect vibrationally excited states in the mercury photo-sensitized reaction. Most of the excess energy is transferred into internal vibrations, especially in the bending mode to compensate a drastic change from the linear to cis-bent structure, because the excess energy is just less to produce the second electronic excited state at the *cis* -configuration and neither strong rotational excitation nor translational acceleration is expected through this spin transfer reaction. This means that a nascent product of the reaction is highly vibrationally excited beyond *cis -trans* barrier in the T_1 potential. That is what we are looking for as a *cis -trans* isomerizing state.

Anyway in the hot band survey experiment, 1-1 band and 1-0 band of C_2H_2 were observed by time-resolving spectroscopy using a less short gate setting just after a pulsed excitation. An effect of the vibrational excitation on the T_1 and T_2 potential will be discussed.

CLASSICAL TRAJECTORY AND STATISTICAL PHYSICS PARTITIONING IN THE PHASE SPACE OF CO_2–Ar

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Weak intermolecular interaction among isolated molecules in a gas results in the formation of true bound, quasibound, and free pair states. The expected spectroscopic manifestations of molecular pairs belonging to these distinct domains of states are essentially different. Rigorous definition of the corresponding statistical weights is therefore worthwhile in the interests of accurate consideration of absorption, emission, or light-scattering phenomena in molecular pairs.

Present paper aims at examination of two possible approaches to subdivision of pair states in the phase space. Statistical analysis of classical trajectories using a sophisticated intermolecular potential allows for discrimination between free collisional pairs and virtually quasibound complexes. The details of intermolecular potential energy surface affecting the formation and parameters of the Feshbach resonances are discussed. An alternative approach which uses statistical physics partitioning in the phase space makes it possible to demarcate the border between true bound and quasibound domains of states. The advantages and shortcomings appropriate to both approaches are discussed in the present paper taking CO_2–Ar weakly interacting system as an example.[a]

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THEORETICAL INVESTIGATION OF THE LOWEST-LYING STATES OF TRANSITION METAL MONOHALIDES LACl AND YI

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Transition metal monohalides are of particular interest in high temperature chemistry. Furthermore, due to the simple open d shell configuration: [core] (n-1)d^1ns^2 of Group IIIA transition metals, their monohalides may be considered as model systems for studying the role of d electrons in chemical bonding. Nevertheless theoretical data are scarce for lanthanum and yttrium halides which have been investigated recently in our Lab (LASIM, Lyon) from high resolution spectroscopic techniques. So, in tight connection with these experimental studies, we have undertaken a systematic theoretical investigation including spin-orbit effects of the low-lying states of LaX and YX with X =F, Cl, Br, I using a CAS-SCF/MRCI approach. Our results for the first species we studied: LaF and LaI were seen to be of good quality when compared with highly accurate experimental data. We extend here the scope of our studies to the molecules LaCl and YI. For LaCl, 11 molecular states in the representation $^{2S+1}\Lambda^{(+/-)}$ and 25 molecular states in the representation $\Omega^{(+/-)}$ have been investigated while for YI 15 states $^{2S+1}\Lambda^{(+/-)}$ and 33 states $\Omega^{(+/-)}$ have been considered. Calculated potential energy curves, spectroscopic constants and spin-orbit splittings will be presented for the two molecules and compared with accurate exprimental data when available.

HIGH-RESOLUTION SPECTROSCOPY OF HOBr IN THE FAR- AND NEAR-INFRARED

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Hypobromous acid, HOBr, is an important species in atmospheric chemistry. In the stratosphere it is mainly produced by the reaction between BrO and HO_2 but rapidly photolyzed by sunlight. In the marine troposphere it is also formed by heterogeneous reactions on sea-salt aerosols and is thus involved in the transport of bromine from the oceans into the atmosphere. Attempts to measure atmospheric HOBr concentrations have been made[a] using its far-infrared rotational transitions. In order to provide accurate line positions and intensities in this region we have measured high-resolution Fourier-transform absorption spectra of gaseous HOBr between 100–350 cm^{-1} using the Bruker IFS-120 HR at LPPM in Orsay. We have been able to improve the rotational-vibrational parameters of the ground states[b] and of the ν_3 bands of $HO^{79}Br$ and $HO^{81}Br$ around 620 cm^{-1}. For the rotational line intensities we have taken into account the Herman-Wallis effects. Furthermore, we have measured high-resolution absorption spectra of the $2\nu_1$ bands around 1.4 μm and determined their rotational-vibrational parameters. These overtone bands are observed to be even stronger than the ν_3 fundamental bands, in agreement with *ab-initio* calculations[c]. The results might be useful for detection of atmospheric HOBr using Cavity Ring-Down Spectroscopy with telecommunication diode-lasers operating at room temperature.

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FTS SPECTRA OF ISOTOPOMERS OF THE HYDROGEN SULFIDE IN THE INFRARED REGION

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High-resolution infrared spectra of isotopomers of hydrogen sulfide have been recorded in the 800-6000 cm^{-1} range with the Fourier Transform spectrometer built in GSMA laboratory (Reims, France)[1] , which operates in stepping mode like Connes'type interferometer.[2] The primary aim of this work was to study the isotopic behavior of intensity anomalies previously found through observations ([3] and refs therein) and global calculations [4-5]in the spectra of the major isotopomer $H_2{}^{32}S$. To assign lines of three isotopomers H_2S, D_2S and HDS various mixtures of the these isotopomers are used. An iterative method of accurate quantification of partial pressures of deuterium containing isotopomers will be discussed. Experimental line intensities of hydrogen sulfide isotopomers have been determined at several selected interval (10 μm and 5 μm) by multispectrum fitting technique [6] and further measurements are in progress in the recorded spectral range.

Another objective of this work was to examine a validity of recently determined dipole moment [4-5] and potential energy [7] functions and of related global isotopical spectra predictions [5] for the hydrogen sulfide. First comparisons of our experimental records for D_2S and HDS with simulated spectra made from previous global predictions [5] in the 5 μm region show a good agreement between observations and theory.

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HIGH RESOLUTION FTIR SPECTROSCOPY ON CH_2DI AND CHD_2I: EVALUATION OF THE GROUND STATE CONSTANTS AND ANALYSIS OF THE ν_3 BANDS

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The vibration-rotation properties of methyl halides have long been a subject of great interest. In our group the C_{3v} symmetric top varieties of methyl iodide (CH_3I, $^{13}CH_3I$ and CD_3I) have been thoroughly investigated, see e.g. (1,2) and references therein. There is further interest in studying isotopically substituted species, which do not maintain the C_{3v} symmetry, and on which the high resolution infrared studies are relatively few in the literature.

We have initiated a high resolution study of all the fundamental vibrational bands of the two asymmetric species CH_2DI and CHD_2I. As the first step, the present investigation reports the ground state rotational constants of the two molecules. The constants have been determined from the infrared spectra of the lowest fundamental bands ν_3 (C – I Stretch) using the method of "Ground State Combination Differences". The upper levels of the ν_3 bands turned out to be isolated from other vibrational levels and thus these bands could be treated as unperturbed asymmetric rotor bands: hybrid a/b-type band for CH_2DI and hybrid a/c-type band for CHD_2I.

In case of CH_2DI more than 3100 a-type and 600 b-type rotation-vibration transitions have been assigned to the ν_3 band. In addition, 16 pure rotational transitions from literature (3) have been included. For CHD_2I about 3000 a-type and 80 c-type transitions have been assigned so far. Current best estimates of the ν_3 band centers and some of the ground state rotational constants (all in cm^{-1}) are given in the following table:

	CH_3I	CH_2DI	CHD_2I	CD_3I
A_0	5.1739358	3.9962646(5)	3.1595227(100)	2.5962779
$\frac{1}{2}(B_0 + C_0)$	0.25021563	0.23122939(3)	0.21520996(69)	0.20148265
ν_3	533.216836	518.756420(18)	508.789777(12)	501.115860

The corresponding constants of the symmetric top species CH_3I and CD_3I are given in the table for comparison (4,1).

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THE C–H BENDING VIBRATION ν_4 OF CHLOROFORM $CH^{35}Cl_3$

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In our series of high resolution studies on the infrared spectrum of chloroform we had recently a work[a] dealing e.g. with the C–H bending overtone $2\nu_4$. Both the parallel and perpendicular components were analyzed. Now the continuation includes the fundamental band ν_4. The detailed analysis of the fundamental may also bring new information on the Fermi resonance problem between the C–H streching vibration and the first overtone of the C–H bending[a].

The Fourier transform infrared spectrum over the ν_4 region around 1220 cm^{-1} was measured with the Bruker IFS 120HR spectrometer in Oulu. We applied again the monoisotopic $CH^{35}Cl_3$ sample obtained from Prof. Bürger's laboratory in Wuppertal. The sample pressure was 0.063 Torr and an absorption path length of 3.2 m was used. The instrumental resolution was 0.0018 cm^{-1} and the total recording time of 640 scans was 42 hours.

The difficult structure of the band is dominated by about 25 strong unresolvable band heads on the R–side. The P–side is at first sight a dense forest of blended lines without any regularities. However, series of lines corresponding to K sub-bands could be found there with the aid of a Loomis-Wood program. The assignments cover the range $K = 1 - 65$ and in addition to ${}^{P}P_K(J)$ line series they include some ${}^{P}Q$ branches. On the R side the assignments thus far are limited to the lowest K and J values. The start of the analysis was essentially based on the predictions from the overtone bands. The rough value for ν_0 is 1220.333 cm^{-1}. The preliminary results e.g. for $B_4 - B_0$ and for $(C\zeta)_4$ are close to the predicted values.

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THE ν_1 AND ν_3 INFRARED BANDS OF $^{12}C_2HD$ AND $^{13}C_2HD$ OBSERVED BY FOURIER TRANSFORM SPECTROSCOPY

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The infrared spectrum of $^{12}C_2HD$ $^{13}C_2HD$ has been observed between 2300 and 3500 cm^{-1} by Fourier transform spectroscopy. The ν_1 and ν_3 absorption bands (previous work, Baldacci *et al.*, J. Mol. Spectrosc. **59**, 116(1976)) and the associated hot bands have been investigated.

ANALYSIS OF THE $\nu_7 + \nu_9$ BAND OF DICYANOACETYLENE (NC-CC-CN)

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The $\nu_7 + \nu_9$ (u-g) band of dicyanoacetylene was observed as a very weak band near 368 cm^{-1} below the $\nu_6 - \nu_9$ (g-u) band complex investigated previously [a]. A multireflexion cell with an effective pathlength of 125 m was used [b] and the sample pressure was 123 Pa. The Bruker IFS 120 spectrometer operated at a resolution of 0.0012 cm^{-1} with a He-cooled bolometer detector.

The main $\nu_7 + \nu_9$ (e) transition was observed at 367.95662(3) cm^{-1} in agreement with a less accurate prediction from hot bands in the ν_9 band complex [c]. A total number of 38 line series (including e- and f-components) have been observed, involving different excited levels of $n\nu_7$ and $m\nu_9$ with n up to 3 and m up to 8. The identification of the weaker bands was facilitated by predictions both in wavenumber and in intensity from the ongoing global analysis of dicyanoacetylene.

The global rovibrational analysis programs for sixatomic molecules have been adapted from programs for pentatomic molecules [d]. The model (scheme of anharmonic interactions) will be discussed and preliminary results will be given.

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HIGH RESOLUTION SPECTRUM OF CH_3D IN THE REGIONS OF 3950 - 4600 AND 5700 - 6150 CM^{-1}: ROTATIONAL ASSIGNMENT AND PRELIMINARY ANALYSIS

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The spectroscopy of the deuterated methane isotopomers is of fundamental importance for understanding and improving full-dimensional potential energy and electric dipole hypersurfaces [1,2].

High-resolution (instrumental bandwidth $\Delta\tilde{\nu}$= 0.005 cm^{-1}, FWHM), FTIR spectra of CH_3D in the regions 3950 - 4600 and 5700 - 6150 cm^{-1} were recorded with the BOMEM DA002 spectrometer in Zurich, using a long path cell with the path length set to 14 m, and sample pressures of 2 - 5 mbar.

The assignment of ro-vibrational structures of the recorded spectra was performed by means of ground state combination differences. Totally, more than 2900 transitions were assigned to 15 relatively strong vibrational bands. The maximum J value achieved was $J^{max.}$ = 12 -15 for different bands. Upper state ro-vibrational energies were determined within accuracies of 0.0003 - 0.0005 cm^{-1}.

Numerous irregularities caused by strong resonance interactions can be seen in the spectra. However, because of the absence of reliable values of high order potential constants of the methane molecule, both a definite vibrational assignment as well as reliable fits of the assigned ro-vibrational transitions is not possible at the moment. On the other hand, the present information on vibrational levels is highly valuable in order to test and to improve the potential energy hypersurface of this important molecule, which is the aim of our current and future investigations. The experimental observation and assignment , besides being a first step towards the full analysis, is also of relevance for the spectroscopy of the atmosphere of the Earth and other planets of the solar system.

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ANALYSIS OF THE FIRST HIGH RESOLUTION FT INFRARED SPECTRA OF $F_2{}^{11}BOH$: THE ν_5, ν_8, ν_9, $2\nu_9$ $\nu_8+\nu_9$, AND ν_4 BANDS

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The reactive F_2BOH molecule was first detected by microwave spectroscopy [a], and very recently observed by matrix IR spectroscopy [b]. We report here the first high resolution infrared study of F_2BOH together with new microwave measurements. This has been produced in a slow flow of (^{11}B, ^{10}B and natural) BF_3 through a glass tube filled with some specks of quartz (or using stainless steel equipment) on which water had been deposited. The ground state rotational spectrum of $F_2{}^{11}BOH$ was measured between 200 and 400 GHz. 156 millimeter-wave transitions combined with 17 microwave transitions (previously measured) and 3896 GCSD allowed us to obtain accurate rotational and centrifugal distortion constants up to sextic terms. As F_2BOH is an oblate top, the representations Ir and IIIr and compared. It is also checked that the A- and S-reductions give results of comparable quality. The IR spectrum has been recorded from 400 cm^{-1} to 1600 cm^{-1} at high resolution (2-3 x 10^{-3} cm^{-1}) using the Wuppertal Bruker 120 HR interferometer equipped with a cell of 1.2 m path length. Among the recorded infrared bands, one B-type out-of-plane ν_5 (BF_2 bend) two c-type out-of-plane fundamental bands ν_8 (BF_2 bend) and ν_9 (OH torsion) and the A-type $\nu_8+\nu_9$ band located at 880.74cm^{-1}, 684.16 cm^{-1} and 522.86 cm^{-1}, 1213.011 cm^{-1} respectively, were analysed using a simple Watson -type Hamiltonian. The a/b type hybrid $2\nu_9$ and ν_4 bands centered at 1042.87 and 961.49 cm^{-1} were also studied. The analysis of ν_4 (OH bending mode) was complicated by the existence of "classical" vibrational rotational resonances linking the 4^1 energy levels with those of the 7^19^1 dark overtone state. More surprising is the fact that both in the $2\nu_9$ and ν_4 bands, the P- and R-lines exhibit a regular doublet structure (of about 0.005 and 0.003 cm^{-1} respectively) which indicates the existence of large amplitude motions in the F_2BOH molecule.

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FIRST HIGH-RESOLUTION FTIR ANALYSIS OF THE ν_9 BAND OF CH_2DF AND CONNECTION WITH THE NEAR ν_5 AND ν_6 VIBRATIONAL LEVELS

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The infrared spectrum of the isotopic form of methyl fluoride CH_2DF has been recorded at high resolution (0.004 cm^{-1}, unapodized) in the range 800 - 1200 cm^{-1}, using a Bomem DA3.002 Fourier transform spectrometer. CH_2DF is a near prolate asymmetric top molecule (asymmetry parameter $\kappa = -0.978$) belonging to the point group C_s, with the a and b axis lying in the molecular-symmetry plane and the c axis perpendicular to it.

This contribution reports the assignment of the rovibrational structure of the ν_9 fundamental ($\sim$ 1133 cm^{-1}) which exhibits an anomalous envelope. This vibration of A'' species, expected to give a pure c-type profile, shows instead a structure which looks like a special a-type envelope following the ΔK_a=0 and ΔK_c=0, $\pm$2 selection rules. Its intensity is derived from strong a-type Coriolis interaction with the near vibrational level ν_5, which is in turn perturbed by ν_6. The ν_5 ($\sim$ 1055 cm^{-1}) and ν_6 ($\sim$ 938 cm^{-1}) vibrations, of A' species, give rise to bands with predominant a-type component although, in principle, they both should be a/b-hybrid bands. During the line assignment further apparent irregularities, as a large unexpected asymmetry splitting involving the upper sublevels with $K_a = 5, 6$ in ν_5 and some local crossings in ν_5 and ν_6, have been observed.

The three bands have been analyzed using a triad model taking into account the main resonances. The transitions have been fitted to the Watson-type Hamiltonian (A-reduction and I^r representation), fixing the ground state parameters at previously determined values (1). A satisfactory fit has been obtained by including a/b-type Coriolis coupling parameters between ν_5 and ν_9 and c-type Coriolis and high-order vibrational interaction terms between ν_5 and ν_6.

The analysis provided the identification of about 200 transitions for the weaker ν_9 band ($J \leq 24$, $K_a \leq 10$), 1200 for ν_5 ($J \leq 37$, $K_a \leq 13$) and 600 for ν_6 ($J \leq 27$, $K_a \leq 10$). From this study an accurate set of upper state constants for ν_9 has been determined for the first time, while the molecular parameters of ν_5 and ν_6 represent a satisfactory improvement with respect to the previous analysis (2).

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HIGH-RESOLUTION ABSORPTION SPECTRA OF ISOTOPIC SPECIES OF CARBON DIOXIDE CONTAINING ^{13}C

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The absorption spectra of ^{13}C enriched carbon dioxide has been recorded in the spectral range of 4000 – 9500 cm^{-1} with a Bruker IFS 120HR Fourier-transform spectrometer equipped with a path length adjustable (maximum 105m) multi-pass gas cell. As stated by Aldrich Chemical Company, Inc., the sample contains 99% of ^{13}C atoms, and 6% of ^{18}O atoms. A minor amount of $^{16}O^{13}C^{17}O$ is also found as evidenced in the experiment. Because of the wide spectral range and the large variation of the absorption line intensities, several measurements were carried out under different experimental conditions. The accuracy of line positions of unblended lines was estimated to be better than 0.001 cm^{-1}. Seven new hot bands of $^{13}C^{16}O_2$, eight new bands of $^{16}O^{13}C^{18}O$, and five new bands of $^{16}O^{13}C^{17}O$ have been observed.

The new observations together with data collected from the literature have been used to fit parameters of an effective Hamiltonian [1] for the$^{16}O^{13}C^{18}O$ isotopic species of carbon dioxide. The data set consists of 4170 line positions of 37 bands. They have been reproduced with an RMS deviation of 0.001 cm^{-1} using 61 effective Hamiltonian parameters.

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ROVIBRATIONAL ANALYSIS OF THE ν_4 AND THE $\nu_5 + \nu_9$ BANDS OF $CH^{35}Cl_2F$

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$CH^{35}Cl_2F$ and its chiral isotopomer $CH^{35}Cl^{37}ClF$ are of some importance for the Earth's atmosphere and in relation to isotopic parity violation[a,b]. For that reason the rovibrational spectra of $CH^{35}Cl_2F$ and $CH^{35}Cl^{37}ClF$ have been already analysed by Snels and Quack[c] with respect to the ν_8, ν_3 and ν_7 fundamental bands ($\Delta\nu = 0.004$ cm^{-1}).

With our new Fourier transform infrared (FTIR) spectrometer Bruker IFS 120 HR (very high resolution prototype) we are now able to measure rovibrational spectra with a resolution up to 0.0007 cm^{-1}. Using these high resolution spectra we have now analysed the weak transitions of the ν_4 and $\nu_5 + \nu_9$ bands of $CH^{35}Cl_2F$. The lines have been assigned with the help of the Giessen Loomis-Wood program. Local resonances have been detected in the ν_4 band. Both bands including the reassigned ν_7 band have been fitted together to an effective Hamiltonian with a standard deviations of $d_{rms} = 0.0003$ cm^{-1} . The fit leads to improved spectroscopic constants of the ground state.

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HIGH-RESOLUTION FAR-INFRARED FOURIER-TRANSFORM ABSORPTION SPECTROSCOPY OF THE CIS- AND TRANS-ISOMERS OF NITROUS ACID (HONO) AND ITS DEUTERATED ISOTOPOMERS (CIS- AND TRANS-DONO)

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Nitrous acid (HONO) is an important source for tropospheric OH. However, the chemical mechanisms for the heterogeneous production of HONO are still not well established. In order to improve the spectroscopic knowledge of this molecule, we have recorded the far-infrared absorption spectrum (20-650 cm^{-1}) with an apodized resolution of 0.003 cm^{-1}. The HONO was prepared directly in a 1-meter long multiple reflexion Pyrex cell by mixing H_2O, NO, and NO_2. The optical pathlength used was 800 cm. We have observed the pure rotational spectra of the *cis*- and *trans*-isomers of HONO and DONO up to high values of J and K_a as well as several low-lying far-infrared bands.[a] First results of the analysis of these high-resolution spectra, starting with predictions based on previous studies in the mid-infrared spectral region[b,c,d] will be reported.

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[c]J. M. Guilmot, M. Godefroid, and M. Herman, *J. Mol. Spectrosc.* **160**, 401-410 (1993).
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NEW ANALYSIS OF THE ν_2, ν_3, ν_4 AND ν_6 BANDS OF FORMALDEHYDE $H_2{}^{12}C^{16}O$. LINE POSITIONS AND INTENSITIES IN THE 5-10 μm SPECTRAL REGION

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This work, besides its fundamental interest, is mainly motivated by the atmospheric importance of formaldehyde. The 10μm region is indeed a possible spectral domain for the detection of this molecule in the atmosphere and no line parameters are presently available in the atmospheric databases for H_2CO in this spectral range. Using the experimental data available in the literature for the ν_3, ν_4 and ν_6 bands [a], and for the ν_2 band [b], and adequate theoretical models, it proved possible to reproduce satisfactorily the experimental data and to generate a list of line positions and intensities for the 5-10μm region. The Hamiltonian model accounts for the various Coriolis-type resonances which perturb the energy levels of the 3^1, 4^1 and 6^1 vibrational states as well as for the weaker anharmonic resonances coupling the 2^1 and 3^1 energy levels. This is also the case for the line intensity calculations which allow one to reproduce satisfactorily the line by line intensity measurements as well as the integrated intensities available in the literature.

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Invited Lectures E

Tuesday, September 9, 9:00

Chairman : R. ZARE

FOURIER TRANSFORM INTRACAVITY LASER ABSORPTION SPECTROSCOPY *(20 min.)*

DANIEL HURTMANS, *Service de Chimie Quantique et de Photophysique (formerly Laboratoire de Chimie Physique Moléculaire), Université Libre de Bruxelles, CPi 160/09, 50 Av. F.D. Roosevelt, B-1050 Bruxelles, BELGIUM*

Intracavity laser absorption spectroscopy (ICLAS) is based on a laser operated in transient regime leading to a broadband multimode emission with a sample cell inserted inside the cavity. As the laser modes are building up, the intracavity absorption increases. Recording absorption at time t_g (generation time) after switching the pump laser on, allows the equivalent absorption path length inside the sample to become $\ell_{eq} = (\ell/L)ct_g$, with ℓ and L the resonator and cell lengths, respectively, and c the speed of light.

This technique, first described in the early 70's [1] is mainly based on Ar^+ pumped Ti:Sapphire lasers, covering the NIR region (e.g. [2,3]); dye lasers in the visible and UV range (e.g. [4,5]); and more recently VECSEL lasers giving access to the lower energy range (e.g [6]), down to around 9500 cm^{-1}, so far. The spectra were mainly recorded using grating spectrometers.

In 1991, the Madrid group demonstrated the feasibility of a set-up combining ICLAS sensitivity and FTS advantages [7]. Similar experiments were since performed by few groups, starting in 1997 [8], and more recently in Hefei [9], Orsay [10] and Brussels [11].

In this paper, we will present the instrument recently developed in Brussels. It consists in a home made Titanium-doped Sapphire laser, developed on purpose for this experiment, linked to a continuous scan Fourier transform spectrometer (Bruker IFS120/HR) equipped with time resolved (TRS) facilities and requiring dedicated synchronization procedures. With this new system and using a generation time of 250 μs, an equivalent path length of 45 km can be obtained. A two generation times technique, previously reported with "conventional" ICLAS [12] for removing seeding noise, was successfully

applied. Selected examples will illustrate the technique.

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12 V. R. Mironenko and V. I. Yudson, *Opt. Commun.* **34**, 397 (1980)

CAVITY ENHANCED ABSORPTION SPECTROSCOPY, FROM DIODE LASERS TO MODELOCKED LASERS *(20 min.)*

D. ROMANINI, J. MORVILLE, T. GHERMAN, S. KASSI, N. SADEGHI, A. CAMPARGUE, and M. CHENEVIER, *Laboratoire de Spectrométrie Physique – CNRS UMR5588, Universit de Grenoble – Saint Martin d'Hères Cedex, France*

Cavity Enhanced Absorption Spectroscopy (CEAS) exploits the long residence time of photons circulating inside a high finesse optical cavity. Radiation transmitted by the cavity is attenuated when its wavelength coincides with an absorption line of a species present inside the cavity: Actually, sample absorption is strongly enhanced, by a factor close to the cavity finesse. We will present two CEAS schemes adapted to different laser sources.

The first CEAS scheme works with a diode laser, and exploits its sensitivity to optical feedback (OF) for efficient injection of the successive modes of a cavity as the laser is tuned. We realized a compact device giving high quality OF-CEAS spectra of an isolated absorption line with up to 50 Hz repetition rate, which is very interesting for application to trace detection.

The second CEAS scheme works with a modelocked (ML) femtosecond laser, whose comb of modes is matched to the comb of transmission modes of the cavity. A spectrograph equipped with a CCD is used to observe the spectrum transmitted by the cavity. We exploited this ML-CEAS scheme to obtain broad band high–resolution spectra with a frequency–doubled Ti-Sa laser in the region around 400 nm. The performance is comparable to that of ICLAS (Intra-Cavity Laser Absorption Spectroscopy) in particular with respect to the ability of providing multiplexed spectral measurements. Even though the acquisition time appears to be longer (for the same sensitivity), a clear advantage with respect to ICLAS is the possibility to access the blue and UV spectral region thanks to the efficient harmonic frequencies generation from ultrashort–pulse lasers.

Ar··· I_2: A MODEL SYSTEM FOR COMPLEX DYNAMICS *(45 min.)*

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The Ar···I_2 Van der Waals complex constitutes a prototype for a wide range of molecular processes: vibrational predissociation involving intramolecular vibrational relaxation, electronic predissociation, cage effect... Each of these processes has been or still is the subject of differing interpretations: intramolecular vibrational relaxation involved in the vibrational predissociation of this system can be in the sparse or statistical regime, vibrational and electronic predissociation are in competition, and a direct, ballistic interpretation of the cage effect as well as a nonadiabatic one have been proposed. The study of the dependence of these dynamical processes on the relative orientation of the two partners of the complex (stereodynamics) is made possible by the coexistence of two stable Ar···$I_2(X)$ isomers.

We present spectroscopic and photodissociation dynamical studies in the region of the $B \leftarrow X$ transition of the Ar···I_2 Van der Waals complex, both below and above the dissociation limit of the $B(^3\Pi\, 0_u^+)$ state. We review experimental as well as theoretical results, and present a new interpretation of the competition between electronic and vibrational predissociation, based on recent three-dimensional nonadiabatic wave packet calculations including all the relevant excited electronic states and their couplings within the diatomics-in-molecules (DIM) model.

Poster Session F

Tuesday, September 9, 11:00

AMAT MILLS Award Applicant

DECAGONAL QUASIPERIODIC STRUCTURES VIA ATOM-OPTICAL NANOFABRICATION

G. MYSZKIEWICZ, E. JURDIK, J. HOHLFELD, W.L. MEERTS, H. VAN KEMPEN AND TH. RASING, *NSRIM, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, the Netherlands*

We deposit a laser-cooled chromium beam onto a substrate through a quasiperiodic laser standing-wave (SW) tuned above the atomic resonance at the ^{52}Cr transition $^7S_3 \rightarrow {}^7P_4^o$ at 425.55 nm. This SW is created by interference of five laser beams crossing in one point at mutual angles of 72 degrees. The resulting chromium pattern on the substrate surface mimics the geometry of the SW and it is thus itself quasiperiodic. On a surface area of 0.2×0.2 mm^2 the Spatial Fourier spectrum of the measured patterns is decagonal. Besides being of fundamental interest, this quasiperiodic nanofabrication via atom optics can find its applications in photonic manipulation of light.

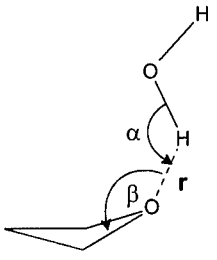
AMAT MILLS Award Applicant

FREE JET ROTATIONAL SPECTRA AND HYDROGEN BONDING: OXETANE-WATER

B. MICHELA GIULIANO, PAOLO OTTAVIANI, BIAGIO VELINO and WALTHER CAMINATI, *Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna (Italy)*

Information on the features of intramolecular hydrogen bond can be obtained from the rotational spectra of complexes formed between organic Lewis bases and proton donors. Here we report the results of the study of the free jet millimeter wave absorption spectrum of oxetane water. From this investigation we obtained a detailed structure of the H bond in the complex. We also performed ab initio calculation at MP2/6-311++G** and B3LYP/6-311++G** level in order to gain geometrical and energetic information.

The shape of the complex and the H bond parameters are given in the figure below.



r_{OH-O}	=	1.853(2) Å
α	=	172(1)°
β	=	112.8(4)°

AMAT MILLS Award Applicant

SPECTROSCOPY OF OCTAHEDRAL MOLECULES IN A DEGENERATE ELECTRONIC STATE: DETAILED INVESTIGATION OF THE 720 cm^{-1} REGION OF JET-COOLED ReF_6

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The Rhenium hexafluoride (ReF_6) molecule has the particularity to possess an incomplete electronic *d* subshell. It also exhibits a very large spin-orbit coupling leading to a fourfold degenerate electronic ground state of symmetry G_g'. Consequently, vibronic and rovibronic-type couplings arise from this particular electronic configuration, which considerably complicate calculations. Recent experimental[a] and theoretical[b,c] work has led to a new analysis[d] of the region around 720 cm^{-1} corresponding to the ν_3 stretching fundamental band (F_{1u} symmetry). Due to a non Born-Oppenheimer behaviour the *PQR*-like pattern expected and actually observed for usual spherical tops such as WF_6[a] is clearly absent in the spectra of ReF_6 which exhibits unconventional broad substructures with very numerous lines. These features thus corroborate the existence of a dynamical quadratic Jahn-Teller effect as proposed by McDowell and Asprey [e] thirty years ago.

Until now, ν_3 was considered as an isolated band but the intensity effects in the simulated spectra above 728 cm^{-1} suggested us that $\nu_2+\nu_6$, around 740 cm^{-1}, could be included to refine the study. So, for the very first time we consider the treatment of the ($\nu_3/\nu_2+\nu_6$) dyad in the quadruplet electronic ground state of ReF_6 through the construction of an effective rovibronic Hamiltonian[c]. This new theoretical model is based on a vibronic polyad scheme, where the Hamiltonian for the considered dyad is written as

$$\tilde{H}^{<\mathrm{Dyad}>} = \tilde{H}^{<\mathrm{Dyad}>}_{\{\mathrm{GS}\}} + \tilde{H}^{<\mathrm{Dyad}>}_{\{\nu_2\}} + \tilde{H}^{<\mathrm{Dyad}>}_{\{\nu_6\}} + \tilde{H}^{<\mathrm{Dyad}>}_{\{\mathrm{Dyad}\}}$$

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[c] M. Rey, V. Boudon and M. Loëte, *J. Mol. Struct.* **599**, 125-137 (2001).

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and allows a simultaneous treatment of the twelve vibronic sublevels $\{F_{1u} \oplus (E_g \otimes F_{2u})\} \otimes G'_g = 3E'_{1u} \oplus 3E'_{2u} \oplus 6G'_u$. Here, we report simulations of the low-resolution band profile as well as some detailed portions at high resolution compared to the jet-FTIR and diode laser spectra.

We also briefly discuss the qualitative correspondence between the quantum and semiclassical energy levels [f,g]. We simply explain the clustering of group representations with large rotational angular momentum and also predict the redistribution of quantum rotational levels thanks to *rotational energy surfaces* (RES). We also analyze statistical properties of experimental and theoretical spectra.

† Present address: ETH Zürich, Laboratorium für Physikalische Chemie, ETH-Hönggerberg, HCI, CH-8093 Zürich, Switzerland.

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[g]D. A. Sadovskii and B. I. Zhilinskii, *Mol. Phys.*, **65**(1), 109–128 (1988).

AMAT MILLS Award Applicant

SURPRISINGLY LARGE PARITY VIOLATING ENERGY DIFFERENCES IN ENANTIOMERS WHICH ARE CHIRAL BY ISOTOPIC SUBSTITUTION: THEORY AND INITIAL SPECTROSCOPIC STUDIES

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Due to the parity violating electroweak interaction, enantiomers of chiral molecules have slightly different energies. Fundamental aspects and consequences of this phenomenon are discussed in ref. [1-3]. In order to measure effects caused by parity violation, it is important to find chiral compounds with a sufficiently large parity violating energy difference and which are suitable for high resolution rovibrational spectroscopy. Indeed, as discussed for instance in [1], the currently pursued approaches towards molecular parity violation by spectroscopy require as a first step a rovibrational analysis of infrared or visible spectra. This requirement must be seen in the light of the fact that until today only few such analyses have been carried out for chiral molecules, all of them pioneered in our research group. We wanted to find out whether the pool of appropriate chiral molecules could be increased by compounds which are chiral only by isotopic substitution like PXY_2 (X,Y = H, D, F, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br) and therefore asked:

- How large is the parity violating energy in molecules which are chiral only by isotopic substitution?
- How strong is the effect on parity violating energy due to structural change caused by isotopic substitution?
- How does vibrational excitation change the parity violating energy in such molecules?

The parity violating energy E_{PV} was calculated with our recently developed multi configuration linear response approach [4]. $PX^{35}Cl^{37}Cl$ (X = H, D, F) molecules show large parity violating energies at the equilibrium structure. These E_{PV} values were compared with the vibrationally averaged expectation value of E_{PV}. In order to get a good approximation for the expectation value, we calculated E_{PV} potential cuts as well as the electronic potential energy surfaces for all one dimensional (1-dim) normal coordinate subspaces.

For these 1-dim subspaces accurate vibrational variational calculations were carried out, which enable us to determine individual contributions to E_{PV} for each 1-dim subspace [5,6]. For the deuterated compounds (PHDX with X= F, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br) it turned out, that the vibrationally averaged parity violating energy can be up to three orders of magnitude larger than E_{PV} at the equilibrium structure due to the induced geometry change by isotopic substitution. We also determined contributions for excited vibrational states. Finally, we shall present some preliminary high resolution spectroscopic results and analyses on these compounds (in particular $PFCl_2$).

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2 M. Quack, *Nova Acta Leopoldina NF*, **81**, 137 (1999).
3 M. Quack, *Angew. Chem. Int. Ed. Engl.*, **114**, 4812 (2002).
4 R. Berger and M. Quack, *J. Chem. Phys.*, **112**, 3148 (2000).
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AMAT MILLS Award Applicant

THE ROTATIONAL SPECTRUM OF THE He-HCCCN VAN DER WAALS COMPLEX: A COMPARISON OF EXPERIMENT AND THEORY

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A high level *ab initio* potential energy surface was calculated for the He-HCCCN van der Waals complex at the CCSD(T) level of theory, using aug-cc-pVTZ basis sets centered on each nucleus supplemented by bond functions. This surface has a global minimum at a T-shaped geometry with a well depth of -37.98 cm^{-1}. Secondary minima exist at both the H- and N-bonded linear configurations, with depths of -29.25 cm^{-1} and -19.33 cm^{-1}, respectively. Hutson's BOUND computer code[a] was used to determine the energies of the bound states supported by the potential energy surface. Twelve rotational transitions were measured in the 7-26 GHz frequency region using a pulsed-nozzle Fourier-transform microwave spectrometer. Both strong *a*-type and weaker *b*-type transitions involving low-J rotational levels were observed, in accord with a T-shaped structure of the complex. In addition, the nuclear quadrupole hyperfine structures due to the presence of ^{14}N ($I = 1$) were resolved and analyzed. The quality of the *ab initio* potential energy surface is evaluated by comparison of the experimental transition frequencies with those from the bound state calculations.

[a]J. M. Hutson, BOUND computer code, version 5 (1993), distributed by Collaborative Computational Project No. 6 of the Science and Engineering Research Council (UK).

AMAT MILLS Award Applicant

THE DOUBLE RENNER EFFECT IN A TRIATOMIC MOLECULE

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We have developed a program for calculating the rovibronic energies for a triatomic molecule in 'double-Renner'-degenerate electronic states.

The electronic energy of a triatomic molecule can be doubly degenerate at linear configurations but split into two non-degenerate components at bent geometries. This is termed the Renner effect. If two different linear geometries are accessible to the molecule and the electronic energy is doubly degenerate at these geometries, we speak about the 'double Renner effect.'

For example, a double Renner effect will occur if the triatomic molecule ABC isomerizes between two linear minima ABC and BCA, and the electronic energy is doubly degenerate at these minima. An example of this is afforded by the two isomers MgNC and MgCN in the $\tilde{A}\ ^2\Pi$ electronic state.

Also ABB molecules can exhibit the double Renner effect. In the $\widetilde{X}\ ^2A''$ and $\widetilde{A}\ ^2A'$ electronic states of HOO, the proton orbits the OO moiety with two equivalent minima on each potential surface at bent geometries. At the two linear geometries HOO and OOH (which correspond to transition states on the potential energy surface) the two electronic states are degenerate as a Π state. The two equivalent minima on each surface are separated by another transition state corresponding to a T-shaped geometry.

Our program can treat both ABC- and ABB-type molecules; the new program has been applied to $\tilde{A}\ ^2\Pi$ MgNC/MgCN, and to HOO in the $\widetilde{X}\ ^2A''$ and $\widetilde{A}\ ^2A'$ states. We present detailed analyses of rotation-bending-electronic wavefunctions aimed at providing further insight into the nature of the double-Renner interaction.

AMAT MILLS Award Applicant

ICLAS-VECSEL: I SPECTRAL CONDENSATION

ELENA BERTSEVA, *Laboratoire de Spectrométrie Physique (associated with CNRS UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint Martin d'Hères, France. Institute of Physics, St Petersburg State University, Petrodvorets, St Petersburg, 198904 Russia*; **ALAIN CAMPARGUE**, *Laboratoire de Spectrométrie Physique (associated with CNRS UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint Martin d'Hères, France*

Vertical External Cavity Surface Emitting Lasers (VECSEL) are ideal amplification media for Intracavity Laser Absorption Spectroscopy in the near infrared region. This compact solid state system has been successfully used for systematic investigations of extremely weak overtone transitions in the 8800-10100 cm^{-1}. However, we noted that, in some experimental conditions, the observed line profiles were clearly asymmetric, this distortion being more pronounced for the strongest lines. Much more spectacular effects were observed when we investigated weak bands of acetylene near 1.03 μm: while the weakest absorption lines appeared superimposed on the baseline as usual in ICLAS, the strongest lines mostly disappeared and were replaced by emission lines slightly blue shifted from the absorption line center. This phenomenon is frequently observed in ICLAS-VeCSEL. This behavior, called "spectral condensation" was, in fact, discovered more than thirty years ago and was studied with atomic transitions and pulsed lasers. This is apparently the first observation of such phenomenon in molecular spectroscopy. Our detection scheme has allowed for the recording of hundreds of spectra in a large variety of experimental conditions. We will present a systematic study of the different factors affecting spectral condensation (pumping rate, generation times, sample pressure, line intensities). Compared to the situation in ICLAS-Ti:Sapphire and ICLAS-dye which are quantitative methods, intensity measurements by ICLAS-VECSEL are complicated by spectral condensation: our investigation has showed that condensation effects may appear (i) for long generation times even at low pumping rate ($\eta < 1.1$), (ii) even with absorption lines with intensities as weak as $10^{-26}\ cm^{-1}/(mol \cdot cm^{-2})$.

TIME-RESOLVED FOURIER TRANSFORM INTRACAVITY LASER ABSORPTION SPECTROSCOPY AROUND 1 μm

F. GUEYE, G. GUELACHVILI, N. PICQUÉ, *Laboratoire de Photophysique Moléculaire, Unité Propre du CNRS, Bâtiment 350, Université de Paris-Sud, 91405 Orsay Cedex*; **V. DANA, J.-Y. MANDIN**, *Laboratoire de Physique Moléculaire et Applications, case courrier 76, Université Pierre-et-Marie-Curie, 75252 Paris Cedex 05, France*

Intracavity laser spectroscopy (ICLAS) is known since long as an efficient technique for the investigation of weak molecular transitions, through the obtention of broadband long absorption path length spectra. Multichannel grating spectrometers have been the traditional tool to measure the ICLAS data. Using Fourier transform (FT) interferometers instead of dispersers represents an interesting alternative. They have been used with titanium-sapphire[a,b] and dye[c,d] ICLAS set-ups, in the visible range (up to 0.82 μm).
This poster will report progress made on the implementation[e,f,g,h,i] of a near-infrared intracavity laser absorption experiment coupled to a stepping-mode time-resolved FT interferometer[j]. Molecular spectra are obtained around 1 μm for absorption path lengths of many kilometers with an intracavity laser absorption set-up based on an optically pumped Vertical Cavity Surface Emitting

[a]S.-M. Hu, A. Campargue, Z.-Y. Wu, Y. Ding, A.-W. Liu, Q.-S. Zhu, High-resolution Fourier-transform intra-cavity laser absorption spectroscopy: application to $^{12}C_2H_2$ near 12300 cm^{-1}, Chem. Phys. Lett. 372, 659-667 (2003).

[b]D. Hurtmans, S. Kassi, C. Depiesse, M. Herman, Assignment of a perturbation in the FT-ICLAS spectrum of $^{12}C_2H_2$ around 12 709.5 cm^{-1}, Mol. Phys. 100, 3507-3511 (2003).

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[j]N. Picqué, G. Guelachvili, High-information time-resolved Fourier transform spectroscopy at work, Appl. Opt. 39, 3984-3990, 2000.

Laser (VCSEL). ICLAS with VCSEL has already been applied successfully to spectroscopic studies with grating dispersers[k]. Combining the two techniques, ICLAS and stepping-mode time-resolved FT spectroscopy, yields specific advantages, especially for frequency and intensity metrology of weak absorption transitions, which are discussed.

[k]Y. Ding, O. Naumenko, S.-M. Hu, Q. Zhu, E. Bertseva and A. Campargue, The absorption spectrum of H2S between 9540 and 10 000 cm^{-1} by intracavity laser absorption spectroscopy with a vertical external cavity surface emitting laser, J. Mol. Spectrosc. 217, 222-238 (2003).

OPTICAL ABSORPTION SPECTROSCOPY OF THE CIRCUMSTELLAR ENVELOPE OF IRC +10216 USING BACKGROUND STARS

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The identification of the carriers of the diffuse interstellar bands is a major challenge in molecular astrophysics. Diffuse band absorptions are generally observed along lines of sight towards heavily reddened stars. In this study observations were undertaken to seek evidence for diffuse band carriers in the localized circumstellar envelope of the carbon star IRC +10216, using optical absorption spectroscopy towards background stars lying behind the envelope. The telescopes/spectrographs VLT/UVES and WHT/UES were used. Analysis using Kurucz model atmospheres and spectral synthesis techniques has been performed for the spectrum of the most favourable target, Star 6, confirming that this star is much more distant than the carbon star envelope. Diffuse band absorptions arising in the circumstellar envelope were not observed, suggesting that if mass-losing carbon stars are the origin of the material that gives rise to diffuse band carriers, then the material must be modified chemically *en route* to the interstellar medium.

THE UIR EMISSION FEATURES OF THE RED RECTANGLE

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We report high S/N UIR emission spectra of the Red Rectangle obtained using CGS4 (3.3 μm region) and MICHELLE (7.7, 8.6 and 11.3 μm etc.) at UKIRT. Use of a long slit allows study of the evolution of the features as a function of distance from the central star through the nebula and towards the conditions of the interstellar medium. Results from the CGS4 data include a remarkable Lorentzian fit to the on-star 3.3 μm feature, and evolution from a Type 2 3.3 μm feature on-star to a broader Type 1 feature with increasing distance into the nebula. This evolution is most readily interpreted in terms of the growth of a separate new emission band centred at 3.28 μm that increases in strength relative to the main 3.3 μm feature, yielding an overall Type 1 shape as commonly seen in nebulae. An absorption feature at 3.28 μm towards the Galactic centre has been reported by Chiar et al. (2000) and may be the absorption counterpart to this emission feature. Results will be presented on the spectral evolution of mid-IR bands recorded using MICHELLE, also as a function of distance.

HIGH-RESOLUTION FOURIER-TRANSFORM INTRA-CAVITY LASER ABSORPTION SPECTROSCOPY: APPLICATION TO $^{12}C_2H_2$ NEAR 12300 cm^{-1}

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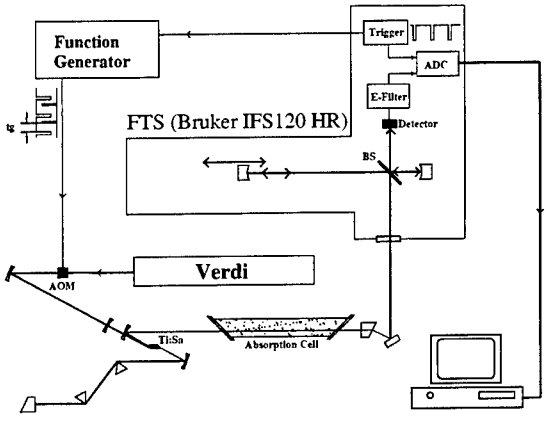
The capabilities of ICLAS associated with a high resolution Fourier Transform spectrometer (FT-ICLAS) are investigated with a Ti : Sapphire laser. In terms of sensitivity, an electric filtering of the FTS signal is showed to decrease significantly the noise level. Weak absorption lines of atmospheric water were used to test the accuracy of absolute intensity measurements by FT-ICLAS leading to an excellent agreement (a few %) with the intensity values obtained by conventional FTS. The performances in terms of spectral resolution (0.028 cm^{-1}) and sensitivity ($\alpha_{min} \approx 2 \times 10^{-9}$ cm^{-1}) are illustrated by the spectroscopic study of the overtone spectrum of $^{12}C_2H_2$ between 12250 and 12400 cm^{-1} which allowed for a significant improvement of recent CRDS measurements. Among the three $\Pi - \Sigma$ bands rotationally analyzed, one is newly observed. The absolute intensity values of the bands are given.

Figure 1. Configuration of the FT-ICLAS set up.



AOM: acousto-optic modulator,
BS: beam splitter,
ADC:analog-to-digital converter,
E-Filter: band-pass electrical filter.

ICLAS-VECSEL: II HIGH SENSITIVITY OVERTONE SPECTROSCOPY OF HDO, H_2O AND ACETYLENE NEAR 1.05 μm

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Intracavity Laser Absorption Spectroscopy based on Vertical External Cavity Surface Emitting Lasers (VECSELs) is an extremely sensitive technique which gives access to the 8800-10100 cm^{-1} spectra region. We have used ICLAS-VeCSEL for line positions measurements in the overtone spectrum of H_2O, HDO and acetylenes.

HDO: Overall 1278 lines were attributed to the HDO species between 9625 and 10100 cm^{-1} and were rovibrationally assigned using both the spectrum predicted by Schwenke and Partridge, and the spectrum simulation performed within the effective Hamiltonian approach. As a result, 289 precise energy levels were derived and modeled for the (102)-(022) resonance dyad and 101 were assigned to the (032), (230), (150), (310), (112), and (080) states.

H_2O: The very weak water vapor absorption spectrum has been analyzed between 9520 and 10010 cm^{-1} leading to the rovibrational assignment of 156 new energy levels belonging to a total of 13 vibrational states. The assignment process performed on the basis of the *ab initio* calculations of Schwenke and Partridge, will be detailed. The results are compared with the available databases and discussed in regard with recent investigations by Fourier Transform Spectroscopy with long absorption paths.

C_2D_2 and C_2H_2: Seven and six bands, most of them newly reported, were analysed for C_2D_2 and C_2H_2 respectively. The spectroscopic parameters retrieved from the rovibrational analyses agree satisfactorily with the predictions of the respective effective Hamiltonian models. The $\nu_1 + 3\nu_3$ band of $^{13}C^{12}CD_2$, present in natural abundance in the sample, could also be detected at 9746.16 cm^{-1} in full agreement with local mode model predictions.

BAND SHAPES IN THE INFRARED SPECTRA OF VAN DER WAALS-BONDED NANOPARTICLES

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The van der Waals-bonded aggregates of nanometric sizes represent the first step towards the condensation of a gas. Situated between gas phase and bulk material, nanoparticles have interesting and specific properties which can be investigated by infrared spectroscopy. The band shapes of their infrared spectra (widths and positions of absorptions, appearance of extra structures and relative intensities of these features) thus contain relevant information about their degree of crystallinity, size, morphology or temperature [a].

Both slit-jet and confined supersonic expansions generated by Laval nozzles combined with central capillary injection [b] have been used to form nanometric particles of different molecules (CO_2, N_2O, C_2H_4). The number of molecules in the aggregate was varied between 2 and about 10^5. A Fourier transform spectrometer (Bruker IFS 120 HR) was used to record the infrared signatures over a wide spectral range.

[a] R. Signorell, *J. Chem. Phys.***118**, 2707 (2003)

[b] A. Bonnamy, R. Georges, A. Benidar, J. Boissoles, A. Canosa and B.R. Rowe., *J. Chem. Phys.***118**, 3612 (2003)

HIGH SENSITIVITY CW-CRDS OF H_2O IN ATMOSPHERIC SPECTRAL WINDOWS

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The characterization of the absorption spectrum of water in spectral regions corresponding to extremely weak transitions is of particular importance as these "atmospheric windows" are used for astrophysics observations or for the search and measurement of other atmospheric species. We have recorded the high resolution absorption spectrum of pure natural water by cw-CRDS in the 6100-6500 and 13310-13380 cm^{-1} spectral regions using a series of DFB diode lasers and a Ti:Sapphire laser respectively. The achieved detectivity is better than $5 \cdot 10^{-10}$ cm^{-1}, improving by at least one order of magnitude the previous measurements performed by FTS associated with long multipass cells [1,2] and leading to the observation of numerous new transitions. We will discuss a comparison of our results to Hitran and other databases [1,2] and with the *ab initio* spectrum calculated by Schwenke and Partridge [3]. The importance of the supplementary absorbance due to the newly detected transitions will be discussed too.

1 P.-F. Coheur et al., *J. Quant. Spectrosc. Radiat. Transfer.*, **74**, 493-510 (2002).
2 R. Schermaul et al., *J. Mol. Spectrosc.*, **211**, 169-178 (2002).
3 D. W. Schwenke, H. Partridge, *J. Chem. Phys.*, **113**, 6592-6597 (2000).

FOURIER TRANSFORM – INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF C_2HD

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We have built an experimental set-up connecting an Ar^+ pumped, home made Sa:Ti laser cavity to a commercial high resolution Fourier transform spectrometer Bruker IFS120HR, to perform ultrasensitive molecular absorption spectroscopy in the near infrared range.[a] We shall report on the experimental technique, demonstrating an effective absorption pathlength of over 40 km and spectral resolution close to 0.005 cm^{-1}. We have applied the technique to study C_2HD.[b] We have recorded spectra from 11800 to 13400 cm^{-1} at two different generation times 35 and 120 μs with about 10 torr of gas (90% purity) at 295 K. New bands have been observed and rotationally analyzed.

We plan to perform a global fit of the vibration-rotation structure in C_2HD. Preliminary results will be reported on.

[a] D. Hurtmans, S. Kassi, C. Depiesse, and M. Herman, Mol. Phys. 100, 3507-3511 (2002)
[b] S. Kassi, C. Depiesse, M. Herman, and D. Hurtmans, Mol. Phys. 101, 1155-1163 (2003)

FREQUENCY MODULATION TRANSIENT LASER ABSORPTION SPECTROSCOPY OF TiS $E^3\Pi$ - $X^3\Delta$

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Transition-metal containing radicals have many low-lying electronic excited states in the visible and near-infrared region and are good candidates for application as photo-catalyst. High-resolution spectroscopy is very useful to study such high spin multiplicity states containing heavy atoms in detail. Absorption techniques are indispensable rather than emission spectroscopy because the photo multiplier tube is less and less sensitive in the longer wavelength region. In this study frequency modulation transient laser absorption spectroscopy was chosen to observe the (0, 0) band of TiS $E^3\Pi$ - $X^3\Delta$ transition in the 7400 cm^{-1} region. This transition is expected to be weak in analogy with TiO. So far this band was only reported by means of FT emission spectroscopy with apodized resolution of 0.05 cm^{-1}.(1) It might be worth pointing out that this band was also found in S-type star.(2) Previous high-resolution studies of this molecule including the other bands have not determined the absolute spin-orbit coupling constants because no satellite bands were reported.

A frequency modulation transient absorption spectrometer was newly built based on the conventional one(3) at the Tokyo Institute of Technology. Modulation frequency of the electro-optical modulator was set at 192.5 MHz. TiS was produced by the reaction of ablated Ti with CS_2 seeded in Argon in jet. Second harmonic of Nd:YAG laser (532 nm 5 mJ/pulse) was used for the ablation. The line width was about 600 MHz governed by Doppler effect. We were able to observe the three main bands of Ω = 0-1, 1-2, 2-3, and the satellite band of Ω = 0-2. Therefore the absolute value of spin-orbit coupling constants should be determined. The detailed analysis will be discussed.

(1) J. Jonsson and O. Launila, *Mol. Phys.* **79** (1993) 95 (2) J. Jonsson, O. Launila, and B. Lindgren, *Mon. Not. R. Astr. Soc,* **258** (1992) 49 (3) A. J. Marr, T. J. Sears, and B.-C. Chang, *J. Chem. Phys.* **109** (1998) 3431

CONCENTRATION MEASUREMENTS OF OZONE IN THE 1200 TO 300 PPBV RANGE: AN INTERCOMPARAISON BETWEEN THE B. N. M. ULTRAVIOLET STANDARD AND INFRARED METHODS

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The LPMA tunable diode laser spectrometer [a], has been equipped with a four channel (one reference beam I_0 and three transmitted beams I_t) data acquisition device and a long path multi-reflection Herriott cell to perform accurate intensity measurements of weak lines. The new data acquisition device retains all the advantages of the stepping recording mode with the Michelson interferometer control of the emitted wavelength of the TDL and allows us to simultaneously record ratios (I_t/I_0) spectra of a reference line and of the line being studied.

A low pressure spectrum of the pure sample given by a short path cell is used as reference spectrum from which the line intensity and instrumental parameters are obtained. The low concentration mixture flows inside the Herriott cell under total pressure of 15 mbar to obtain the infrared spectrum used to derive the concentration value.

In order to compare ozone concentrations derived from infrared absorption measurements to the ultraviolet absorption ones, we use the following configuration. The short path cell is filled with pure distilled ozone while the mixture of ozone in standard air prepared by the 49PS Megatec ozone generator of the B.N.M flows continuously through the Herriott cell. The ultraviolet concentrations given by the B.N.M. ozone generator are calibrated by the N.I.S.T. Standard Reference Photometer using the ultraviolet absorption coefficient determined by A. G. Hearn [b].

In order to improve the accuracy of the concentrations derived from the experimental spectra, a simultaneous analysis is performed by a multi-spectral fitting program taking into account, using the reference spectra, the instrumental effects. The agreement between the two methods is well within the

[a] A. Valentin, Spectrochim. Acta Part A 52, 823-833 (1996)

[b] A. G. Hearn, Proc. Phys. Soc. 78, 932-940 (1961)

absolute uncertainty of each method, and confirms the ultraviolet absorption coefficient value.

The infrared measurements allow to derive a value of the ultraviolet absorption coefficient which can be compare to the value recommended by Hampson (N.I.S.T.).

DEVELOPMENT OF A STABILIZED LOW TEMPERATURE INFRARED ABSORPTION CELL FOR USE IN STANDARD LOW TEMPERATURE AND COLLISIONAL COOLING EXPERIMENTS

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The feasibility of adapting the collisional cooling technique, originally described by De Lucia and co workers, see for example [a], using microwave transitions, to the study of infrared transitions utilizing tunable diode lasers was first demonstrated several years ago by Mantz and co workers [b]

In an effort to improve the accuracy in the determination of spectral line parameters at temperatures as low as 7 K, we have constructed and tested a low temperature cell using the open cycle liquid helium technique. The cell has an absorption path of 16.8 cm. The temperature range over which this cell is actively temperature controlled is 200 K to 7 K. This is illustrated by spectra of carbon monoxide perturbed by argon or helium using the collisionnal cooling technique for the lowest temperatures. The temperature stability of the cell is better than 0.1 K. With this approach the temperature dependence of spectral line parameters can be accurately determined.

In these experiments we use an interferometer controlled multi beam tunable diode laser spectrometer developed at LPMA and recently modified to permit the simultaneous recording of analytical and reference spectra. The simultaneous recording of a reference spectrum with the analytical spectrum overcomes systematic effects coming from the instrument itself and gives the possibility to accurately measure the pressure shift and its temperature dependence. The line and instrumental parameters are determined by a multi-spectra fitting software which incorporates most of the recent line shape models. Results of simultaneous analyses are discussed by D. Hurtmans in an invited paper in which this multi spectral technique is thoroughly described.

[a] J. K. Messer and F. C. De Lucia, Phys. Rev. Lett. 53, 2555-2558 (1984)

[b] D. R. Willey, K. A. Ross, V. Dunjko and A. W. Mantz, J. Mol. Spectrosc. 168, 301-312(1994).

In this poster we will provide a complete description of the cell and some line parameters determined for sample temperatures down to 7 K.

ROTATIONAL AND VIBRATIONAL ANALYSES OF THE MgNC $\tilde{A}\ ^2\Pi$ - $\tilde{X}\ ^2\Sigma^+$ TRANSITION

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We have generated MgNC in supersonic free jet expansions, and measured the laser induced fluorescence excitation spectra of the vibronic bands of the $\tilde{A}\ ^2\Pi$ - $\tilde{X}\ ^2\Sigma^+$ transition. We find some new features in the spectra, though part of the spectra were already reported by Wright and Miller[a]. The new features are consisting of the ν_2 bending vibronic bands. From the rotational analyses of some of the vibronic bands, we have obtained new information on the ro-vibronic structure of the $\tilde{A}\ ^2\Pi$ state of MgNC. The assignment of the ν_2 vibronic bands were carried out by the vibrational analyses of the dispersed fluorescence spectra obtained by the excitation of the ν_2 vibronic bands. On the basis of the vibrational structures of the dispersed fluorescence spectra which also include the spectra obtained by the excitation of the vibronic bands reported by us[b], the vibronic structure of the $\tilde{X}\ ^2\Sigma^+$ state of MgNC have been analysed. The results of the vibronic structures of the MgNC $\tilde{A}\ ^2\Pi$ and $\tilde{X}\ ^2\Sigma^+$ states will be compared with the computational results by Hirano group[c].

[a]R. R. Wright and T. A. Miller, *J. Mol. Spectrosc.* **194**, 219 (1999).

[b]M. Fukushima and T. Ishiwata, *J. Mol. Spectrosc.* **216**, 159 (2002).

[c]T. E. Odaka, T. Taketsugu, T. Hirano and U. Nagashima, *J. Chem. Phys.* **115**, 1349 (2001).

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T. E. Odaka, T. Hirano and P. Jansen, *J. Mol. Spectrosc.* **216**, 379 (2002).

DEPERTURBATION ANALYSIS OF THE $A^2\Pi \sim B^2\Sigma^+$ INTERACTION OF SrBr

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The 2 - 1, 3 - 2 and 4 - 3 bands of the $A^2\Pi$ - $X^2\Sigma^+$ system of $^{88}Sr^{79}Br$ and $^{88}Sr^{81}Br$ have been recorded at high resolution using laser excitation spectroscopy. Selective detection of fluorescence was essential for the acquisition of rotationally resolved branch structure for individual bands of each isotopomer. The $A^2\Pi$ and $B^2\Sigma^+$ states of SrBr exist as a unique perturber pair. Accordingly, in a least squares fit of all known A - X and B - X data for each isotopomer, the global 2^{nd} order effects in the two states (Λ-doubling in the $A^2\Pi$ state and "spin-rotation" splitting in the $B^2\Sigma^+$ state) have been represented essentially by just two electronic interaction parameters, a_{AB} and b_{AB}. Such fits also took account of perturbations arising from local level crossings between $A^2\Pi_{1/2}(v+3)$ and $B^2\Sigma^+(v)$ levels. An unobserved level crossing is predicted to occur between levels of e parity of $v = 2$ and $v = 5$. Reliable deperturbed molecular constants for the low-lying vibrational levels in the A and B states have been obtained. The deperturbed equilibrium bond lengths for the $A^2\Pi$ and $B^2\Sigma^+$ states of SrBr were determined to be 2.71314(9) and 2.71054(2) Å, respectively.

THE [0.25]$X^2\Pi_{1/2}$ SPIN-ORBIT COMPONENT OF NiF

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The ground state electronic configuration of NiF [$Ni^+(3d^9)F^-(2p^6)$] arises three low-lying electronic states: $X^2\Pi_i$, $A^2\Delta_i$, and $B^2\Sigma_i^+$ located in the 0 – 2,500 cm^{-1} energy range above the $X^2\Pi_{3/2}$ ground state. Up to now the $X^2\Pi_{1/2}$ state has not been formally identified, but a state located 251 cm^{-1} above the $X^2\Pi_{3/2}$ state had been assigned as a "$^2\Sigma^+$" state. This "$^2\Sigma^+$" state has an anomalously large spin-rotation constant, γ= -0.960 cm^{-1}, compared to the rotational constant, B= 0.3900 cm^{-1}.

Following the theory developed by Kopp and Hougen[a] and on the basis of the microwave data[b], this state can be described as a $^2\Pi_{1/2}$ state with a Λ-doubling parameter, p, with a value of -1.739 cm^{-1} (*i.e.*, $p = \gamma$ - $2B$). Kopp and Hougen neglected the second order parameters which obey the relationship $p_J = \gamma_D + 4D$.

It turns out that the microwave data can lead to another value of p (p = -0.180 cm^{-1}), which is equally possible, on the basis of only the least-squares fitting of the data. One observes that the difference between the two values of p is equal to $4B$ and that the two associated p_J parameters differ by -$8D$. The final choice in favor of one of the two sets of fine structure parameters (p = -1.739 cm^{-1} and $p_J = 0.201 \times 10^{-4}$ cm^{-1}) can be achieved thanks to the analysis of an electronic transition between the studied state and another already known electronic state[c]. The pattern of the experimental spectrum agrees only with one of the theoretical Fortrat diagrams built on the basis of each of the two possible sets of the fine structure parameters.

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[b] M. Tanimoto, T. Sakamaki and T. Okabayashi, *J. Mol. Spectrosc.* **207**, 66 (2001).
[c] C. Dufour and B. Pinchemel, *J. Mol. Spectrosc.* **173**, 7 0 (1995).

THE VISIBLE SPECTRUM OF CoCl BETWEEN 19,000 AND 23,000 CM^{-1}

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The visible spectrum of CoCl in the 19,000-23,000 cm^{-1} spectral region is made of the overlap of two electronic transitions involving the ground $X^3\Phi_i$ state as stated by Adam *et al.*[b] who applied the technique of laser ablation followed by jet expansion to generate cold CoCl. On our side (Hirao *et al.*[c]) the same transitions were obtained in emission. The light emitted by a DC discharge generated in a 1.2 m-long high temperature tube furnace, was collected on the entrance aperture of a Bruker IFS 120 HR Fourier transform spectrometer. Beside the bands observed by Adam *et al.*[b], we recorded several other features of the two transitions thanks to the high temperature of the source. Subsystems involving the $X^3\Phi_3$ spin-orbit component of the ground state have been recorded for both the transitions and several bands involving the v=1 vibrational levels of the two upper states and of the lower states have been analyzed.

Adam *et al.*[b] identified the two transitions as the $[20.7]^3\Phi_4 - X^3\Phi_4$ and the $[21.3]^3\Phi_4 - X^3\Phi_4$ on the basis of their rotational and hyperfine structures analyses. Presence of strong and well developed Q branches in the $[21.3]-X^3\Phi_i$ transition suggest that this transition is more likely a $\Delta\Lambda \neq 0$ transition rather than a $[21.3]^3\Phi_i - X^3\Phi_i$ transition. The hypothesis of an upper $[21.3]^3\Delta_i$ state is sustained by considerations about electronic configurations of excited states. Based on a conventional N^2-reduced Hamiltonian, the spin-orbit interaction parameters, A_{SO}, are obtained for the $[20.7]^3\Phi_i$ and $[21.3]^3\Delta_i$ states to be -131 and -207 cm^{-1}, respectively, by constraining the value of A_{SO} for the ground state to that of CoF, -233 cm^{-1}.[d]

[b] A. G. Adam, J. R. D. Peers, Ying Teng, and C. Linton, *J. Mol. Spectrosc.* **212**, 111 (2002).

[c] T. Hirao, B. Pinchemel, and P. F. Bernath, *J. Mol. Spectrosc.* **219**, 119 (2003).

[d] A. G. Adam and W. D. Hamilton, *J. Mol. Spectrosc.* **206**, 139 (2001).

PARTITION SUMS AND DISSOCIATION ENERGY FOR $12C16O_2$ AT HIGH TEMPERATURES

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Using the spectroscopic characteristics of a carbon dioxide molecules, we have performed direct calculations of total internal and vibrational partition sums for a basic isotope $12C16O_2$ in a temperature range 400 – 10 000 K with a step of 200 K. The rotational- vibrational states energies are calculated using effective Hamiltonian, taking into account contribution to the Fermi resonance energy. The method of direct summation by states has been employed, taking into account the effect of thermodissociation on the number of the molecule bound states. It has been demonstrated that in order to calculate accurately the partition sum Q at high temperatures, it is necessary to solve combined equations with respect to the partition sum Q as well as the energy of dissociation D_T. The values Q and D_T calculated by means of iterative process are then compared to the results of other calculations [a] [b], which has allowed to estimate the influence of different approximations on the accuracy of the partition sum calculation. It has also been shown that the limitimg of the number of the molecule bound states, resulting from thermodissociation, must be considered at temperatures over 6 000 K. The obtained partition sum values correspond satisfactorily (with an error of about 10%) to those obtained in harmonic approximation in the entire temperature range examined. At the same time, the difference from the calculations [a] exeeds 30% at a temperature of 10 000 K.

1 Thermodinamic properties of certain substances. Reference edition in 4 volumes, edited by V.P. Glushko, Nauka publishing house, 1978, in Russian.

2 R.R. Gamache et al., *J. Mol. Spectrosc.*, **517-518**, 407-425 (2000).

MULTIDIMENSIONAL VIBRATIONAL MODEL FOR 5-METHYLTROPOLONE

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In recent years there is a growing interest in vibronic studies of 5-methyltropolone, a molecule showing a strong coupling between proton transfer with other internal motions, and particularly the internal rotation of a methyl group. The experimental results for S0 and S1 electronic states [a] have been followed by theoretical studies of nuclear dynamics [b]. In the present study a complete symmetry analysis of all vibrational degrees of freedom is presented in the G12 molecular symmetry group. The analysis shows types of rovibrational resonances, which may occur in 5- methyltropolone. The symmetry adapted internal coordinates are used for building a complete vibrational Hamiltonian, which is solved on different levels of approximation. Particular attention is devoted to a proper form of the vibrational potential function, which should rigorously transform according to the fully symmetric irreducible representation. Three and four-dimensional semi-rigid models are applied to explain the dynamics of the molecule and its unusual laser fluorescence excitation spectrum.

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[b] O. Vendrell, M. Moreno and J.M. Lluch J. Chem. Phys. 117, 7525-75332 (2002).

GEOMETRY OF $CaOCH_3$ FROM SPECTRA OF THE $A\ ^2E \leftarrow X\ ^2A_1$ SYSTEM

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Laser excitation spectra of the $A\ ^2E \leftarrow X\ ^2A_1$ system of four isotopomers of calcium methoxide were recorded at the University of New Brunswick. The radicals were produced in a laser ablation source, using a 1.2 % mixture of methanol ($^{12}CH_3OH$, $^{13}CH_3OH$, $^{12}CD_3OD$ and $^{13}CD_3OD$) in He as a precursor. High resolution spectra were recorded in the range 15870 - 15985 cm^{-1} and 16320 - 16500 cm^{-1} (F.W.H.M. 250 MHz) using a tunable, single-mode cw dye laser (CR 699 + autoscan), operating with DCM and Kiton red dyes.

The transitions were assigned to the two spin-orbit components $A\ ^2E_{3/2} \leftarrow X\ ^2A_1$ and $A\ ^2E_{1/2} \leftarrow X\ ^2A_1$ of the origin band, and of a band with v'_4(Ca-[OCH_3] stretch) = 1. Resolved J and K structures are observed. The analysis used an effective Hamiltonian given in the literature[a]. The fits build on earlier work on the main isotopomer[b], and include spectroscopic data for the $B \leftarrow X$ system given in the literature.[cd] We obtain structural parameters for the calcium monomethoxide radical from the rotational constants obtained from the different isotopomers.

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[b]P. Crozet, F. Martin, A.J. Ross, C. Linton, M.J. Dick and A.G. Adam, J. Mol. Spectrosc. 213 28 (2002)

[c]C. J. Whitham, S. A. Beaton, Y. Ito and J. M. Brown, J. Mol. Spectrosc. 191 286 (1998)

[d]K. C. Namiki, J. S. Robinson and T. C. Steimle, J. Chem. Phys. 13 5283 (1998)

GLOBAL FITTING OF VIBRATION-ROTATION LINE POSITIONS OF ACETYLENE MOLECULE IN THE FAR AND MIDDLE INFRARED REGIONS

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Using the effective Hamiltonian suggested in our previous paper [a] the global fitting of vibration-rotation line positions of acetylene molecule in the spectral range 0 - 9000 cm^{-1} has been performed. The effective Hamiltonian is based on the assumption of the cluster structure of vibrational energy levels [b]. A set of 146 effective Hamiltonian parameters, which consists of 88 diagonal and 58 resonance interaction parameters, has been fitted to 7393 line positions of 108 bands, collected from 10 different experimental sources. The root-mean-square deviation of 0.0046 cm^{-1} has been achieved.

1. V.I. Perevalov, E.I. Lobodenko, and J.-L. Teffo, "Reduced effective Hamiltonian for global fitting of C_2H_2 rovibrational lines", in 12^{th} Symposium and School on High Resolution Molecular Spectroscopy, *Proc. SPIE*, **3090**, 143-149 (1997).

2. M. Abbouti Temsamani and M. Herman, *J. Chem. Phys.*, **102**, 6371-6384 (1995).

DETERMINATION OF THE POTENTIAL SURFACE OF H_2O IN THE FRAMEWORK OF THE EXTENDED $SU(2)$ MODEL

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The vibrational description of $H_2\,{}^{16}O$ in terms of Morse local oscillators for both bending and stretching degrees of freedom is presented. Expansions of the kinetic and potential energies of the vibrational Hamiltonian are considered up to quartic terms. The local Morse coordinates y_i as well as the momenta p_i are thereafter expanded in terms of creation and annihilation operators of the Morse functions keeping terms up to order $1/\sqrt{k}$ (up to quadratic terms in the operators), where k is a parameter related with the depth of the potential. Only terms conserving the polyad are considered. The resulting Hamiltonian comprises the known Darling-Dennison and Fermi-like interactions, but unlike the description in terms of a harmonic basis, all the force constants up to quartic order appear. An energy fit is carried out for 72 experimental energies up to $23,000cm^{-1}$, obtaining an rms deviation of 4.99 cm^{-1}. The force constants are determined and predictions for the isotopes $H_2^{17}O$, $H_2^{18}O$, $D_2^{16}O$, and $T_2^{16}O$, are presented.

$SU(4)$ IN ELECTRONIC SPECTROSCOPY OF MOLECULES WITH AN ODD NUMBER OF ELECTRONS

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Various realizations of the $su(4)$ algebra offer new insights into the study of some degenerate electronic states [a].
Two particular chains and their bosonic realization allow the construction of all electronic operators needed for the study of vibronic and rovibronic interactions in a $G'(\Gamma_8)$ state. The first chain

$$\begin{array}{ccccccccc} u(4) & \supset & su(4) & \supset & sp(4) & \supset & su(2) & \supset & X \\ [1\dot{0}] & \downarrow & [1\dot{0}] & \downarrow & \langle 10\rangle & \downarrow & \frac{3}{2} & \downarrow & p \end{array}$$

gives the natural $\frac{3}{2} \downarrow G'$ subduction and is the most convenient from a practical point of view (X is $so(2)$ when dealing with a standard basis (p=m) or G^S the molecular symmetry group with its spinor representations ($p = G', \sigma$)). The second chain

$$\begin{array}{ccccccccccc} u(4) & \supset & su(4) & \supset & so(4) & \approx & su(2)_S & \oplus & su(2)_\Sigma & \supset & X \\ [1\dot{0}] & \downarrow & [1\dot{0}] & \downarrow & & & (\frac{1}{2} & , & \frac{1}{2}) & \downarrow & p \end{array}$$

recovers the well-known pseudo-spin formalism (X is $so(2)_S \oplus so(2)_\Sigma$ or G^S).
In both cases the connection with the Dirac's algebra may be established.
For octahedral molecules vibronic and rovibronic chains will be given for the $G' \otimes F$, $G' \otimes E$ cases. The $E \otimes E$ case will also be outlined.

[a] F. Michelot,M. Rey and V. Boudon J. Mol. Spectrosc., in press (2003).

THE SPECTRUM OF SINGLET SiH_2

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We report here a theoretical study of the $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$ electronic states of silylene SiH_2. These states become degenerate as a $^1\Delta_g$ state at linear configurations and are subject to the Renner effect. In high-level CASSCF/MR-CI + CASPT2 *ab initio* calculations, we have determined the potential energy surfaces and the dipole moment and transition moment surfaces for the two states. Parameterized analytical functions have been fitted through the various sets of *ab initio* points, and the parameter values for the potential energy surfaces have been further refined in simultaneous fittings to experimental spectroscopic data and *ab initio* points. In these fittings, we achieve refined potential energy surfaces that behave reasonably also in regions of configuration space that are not sampled by the wavefunctions of the experimentally characterized states. The calculation of rovibronic energies, the fittings to experimentally derived energies, and simulations of $\tilde{X}^1A_1 \leftarrow \tilde{A}^1B_1$ emission spectra of SiH_2 have been carried out with the RENNER program system[a]. The higher excited vibrational states of $\tilde{X}^1A_1$ -state SiH_2 form polyads of heavily interacting states and many polyad states have been observed in dispersed fluorescence studies. The present theoretical work shows that owing to the heavy interaction between the states in the polyads, it is difficult to obtain unambiguous assignments for these states.

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ROVIBRONIC ENERGY LEVEL STRUCTURE OF THE ETHYLENE RADICAL CATION

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The rovibronic energy level structure of the $\tilde{X}\ ^2B_3$ ground electronic state of the ethylene radical cations $C_2H_4^+$ and $C_2D_4^+$ was studied by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy using single-photon excitation from the neutral ground vibronic state. The spectra in the wavenumber region 84600-86800 cm^{-1} show transitions to cationic vibrational levels involving excitations in the ν_2,ν_3 and ν_4 normal modes. A progression in the torsional mode ν_4 up to v_4=5 is observed and can be analyzed in terms of a large amplitude motion in a double minimum potential with a barrier at the planar geometry. The effect of the deviation from the planar geometry on the photoionization dynamics is discussed. High-resolution PFI-ZEKE photoelectron spectra (Γ_{FWHM}=0.09 cm^{-1}) of the cationic ground vibronic state were recorded in which the rotational structure is fully resolved. The adiabatic ionization potential of C_2H_4 is determined to be (84790.46 $\pm$ 0.25) cm^{-1}.

HIGH-RESOLUTION FTIR AND MMW STUDY OF THE $V_4 = 2$ (A_1, E) EXCITED STATE OF $^{14}NF_3$ NEAR 985 CM^{-1}. THE AXIAL GROUND STATE CONSTANTS DERIVED BY THE LOOP METHOD

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The two $v_4 = 2^0$ (A_1, 983.702 cm^{-1}) and $v_4 = 2^{\pm 2}$ (E, 986.622 cm^{-1}) substates of the oblate symmetric top, $^{14}NF_3$, have been analyzed by high-resolution (2.5×10^{-3} cm^{-1}) IR spectroscopy through the $2\nu_4^0$ and $2\nu_4^{\pm 2}$ overtones as well as through the hot bands $2\nu_4 - \nu_4$ starting from the $v_4 = 1^{\pm 1}$ (E, 492.423 cm^{-1}) state. First, transitions of the $2\nu_4^{\pm 2}$ overtone, the $2\nu_4^{\pm 2} - \nu_4^{\pm 1}$ hot band and the previously measured transitions (*1*) of the $\nu_4^{\pm 1}$ fundamental were combined to yield 585 GSCDs differing in K by ± 3 ($K_{max} = 36$). These GSCD were successfully adjusted using the" loop-method" [a] with a standard deviation $\sigma = 0.320\times10^{-3}$ cm^{-1}. A complete set of the hitherto not experimentally known axial ground state constants (C_0 , D_K^0, H_K^0) was derived. Then, a vibrationally isolated model was used, considering $\ell(2, 2)$ and $\ell(2, -1)$ interactions between the $v_4 = 2^0$ and $v_4 = 2^{\pm 2}$ substates. Neglecting the unobserved small $\ell(2,-4)$ and $k(0,6)$ splittings, but accounting for the $\ell(4, 2)$ one within the $k\ell = -2$ level, this model allowed us to fit 2747 IR data (1842 transitions, 905 energies, $J_{max} = 42$, $K_{max} = 39$) with $\sigma_{IR} = 0.353 \times 10^{-3}$ cm^{-1}.

Concommitantly, a MMW technique of spectroscopy (precision 50-100 kHz) was used, providing 86 transitions ($J_{max} = 16$, $K_{max} = 13$) directly measured on the $v_4 = 2$ state. Therefore, the merged fit, refining 28 parameters through the same model, practically conserved σ_{IR} and gave $\sigma_{MMW} = 0.847\times 10^{-6}$ cm^{-1} (25 kHz) .The v and ℓ-dependences of the $v_4 = 2$ excited state parameters were pointed out, giving in particular anharmonicity constants in cm^{-1} as $x_{44} = -0.84176(2)$ and $g_{44} = +0.73014(1)$. The ground state axial constants are (in cm^{-1}): $C_0 = 0.19499250$ (44); $D_K^0 = 3.4343(88) \times 10^{-7}$; $H_K^0 = -1.0335(481) \times 10^{-12}$.

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MILLIMETERWAVE SPECTRUM OF ETHYLENE

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The rotational spectra of deuterated isotopomers of ethylene, $H_2C{=}CH_2$, have already been measured [a]. The parent species in its ground vibrational state, as far as it is concerned, has no rotational spectrum because it has no permanent dipole moment. However, the vibrational states $v_7 = 1$ and $v_8 = 1$ are close in energy (at 948.77 and 939.86 cm^{-1}, respectively) and some allowed transitions between these two states lie in the millimeterwave range.

The ν_7 state is known with an accuracy better than 10^{-6} cm^{-1}) thanks to CO_2 laser sideband spectra [b]. The ν_8 state has been estimated with an accuracy of the order of 10^{-3} cm^{-1}) by combining the $\nu_7 + \nu_8$ band with the hot band $\nu_7 + \nu_8 - \nu_8$, both analysed in F.T. spectra (unpublished results).

The spectrum has been measured from 180 to 500 GHz and 19 transitions have been assigned without ambiguity to ethylene, with a systematic deviation of about -27 MHz from the predictions. A new analysis of the ν_8 state has been performed, including the a-type Coriolis interaction with the ν_6 state, and a good agreement has been obtained.

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MICROWAVE MEASUREMENTS AND UPDATE OF OZONE GROUND STATE PARAMETERS

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In Kiel, the measurements in the centimeter-wave range were performed by means of waveguide Fourier transform microwave spectroscopy. Spectrometers in the ranges 8-18 GHz and 18-26.5 GHz were used, employing sample cells with a rectangular waveguide of length 12 m and a circular waveguide cell of length 36, respectively. The experiments were carried out at ambient temperature and at gas pressures of ca. 0.5-1.0 Pa. Experimental transition frequencies were obtained from a fit analysis of the transient emission signal, assuming a Voigt profile line function and yielding an accuracy of typically 0.1-10 kHz (three standard deviations) for the line center frequency, depending on the strength of the line.

In Lille, 270 lines in the ground vibrational state of the main species of ozone and about 80 lines in the $v_2 = 1$ vibrational state have been observed in the 180-650 GHz frequency range by using either a video-type spectrometer or a frequency modulated one, with various phase-stabilized Backward-Wave Oscillators as sources and a liquid-Helium cooled bolometer as a detector. Most of the lines have been measured with an accuracy better than 50 kHz.

A new improved set of ground state rotation and centrifugal distortion constants of the ozone molecule were determined from a fit of our original data together with previously available microwave and far-infrared rotational transitions in A- and S-reductions. Comparison with previous calculations will be discussed.

MICROWAVE SPECTRUM AND CONFORMATIONAL COMPOSITION OF ALLENYLPHOSPHINE, $H_2C{=}C{=}CHPH_2$

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The microwave spectrum allenylphosphine has been investigated in the 8-62 GHz spectral region. Two conformers exist for this compound. The lone electron pair is *syn-periplanar* with the C=C-P link of atoms in one conformer,and *anti-clinal* in the other form. A full assignment of the microwave spectrum of the more stable *syn-periplanar* rotamer has now been achieved. Its dipole moment has been measured. The high-K_{-1} transitions of the *a*-type *R*-branch lines of the less stable *anti-clinal* conformer has also been assigned. The MW work has been augmented by high-level quantum chemical calculations to determine the energies of the two conformers at the G3 level of theory. They were also useful for a first prediction of the rotational constants and the dipole moment components. Finally, the structure of both conformers has been determined.

THE GROUND STATE ROTATIONAL SPECTRUM OF SO_2F_2

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The experimental spectrum of the ground state of SO_2F_2 has been recorded by three different spectrometers in the $0 - 1$ THz region. The analysis[a] (J up to 99) has been performed with the Watson's Hamiltonian up to sextic terms but shows some limits due to the A and S reductions. Since SO_2F_2 is a quasi-spherical top, it can also be regarded as derived from an hypothetical XY_4 molecule. Thus we have developed a new tensorial formalism in the $\mathbf{O(3)} \supset \mathbf{T_d} \supset \mathbf{C_{2v}}$ group chain[b]. We test it on the ground state of this molecule using the same experimental data[c]. Both fits are comparable even if the formalisms are slightly different. In this poster, we establish a link between the classical approach and the tensorial formalism. In particular, tensorial parameters at a given order of the development are related to the usual ones. Programs for spectrum simulation and fit using these methods are named C_{2v}TDS. They are freely available at the URL:

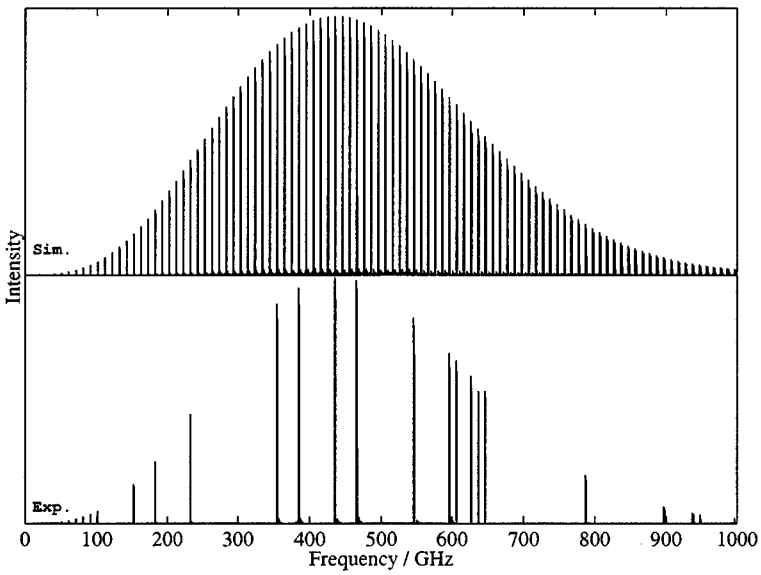
`http://www.u-bourgogne.fr/LPUB/c2vTDS.html`

The figure below shows an overview of the experimental and simulated ground state spectra.

[a] K. Sarka, J. Demaison, L. Margulès, I. Merke, N. Heineking, H. Bürger and H. Ruland, *J. Mol. Spectrosc.*, **200**, 55-64, (2000).

[b] M. Rotger, V. Boudon and M. Loëte, *J. Mol. Spectrosc.*, **216**, 297-307, (2002).

[c] M. Rotger, V. Boudon, M. Loëte, L. Margulès, J. Demaison, H. Mäder, G. Winnewisser and H.S.P. Müller, *J. Mol. Spectrosc.*, submitted, (2003).


Intensity
Sim.
Exp.
0
100
200
300
400
500
600
700
800
900
1000
Frequency / GHz

ROTATIONAL SPECTRUM, HYPERFINE STRUCTURE, AND GEOMETRICAL STRUCTURE OF 2-AZETIDINONE

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2-Azetidinone is the simplest four-membered lactam. There is great biological interest attached to this compound, because it is part of a series of antibiotics such as e.g. penicillins and cephalosporins. The biological activity shown by these antibiotics is presumed to depend on the lactam moiety. The microwave spectrum was already measured in the frequency range 18-38 GHz and an electron diffraction structure was determined (1). In the present work, the quadrupole hyperfine structure due to ^{14}N has been measured using microwave Fourier transform spectroscopy. The rotational constants of the ^{13}C, ^{15}N, and ^{18}O isotopomers have also been determined in natural abundance. An experimental and an ab initio structures have been determined and will be discussed. Finally, the rotational spectra of the ground vibrational state and of the first three excited puckering states have been measured from 8 to 470 GHz and accurate centrifugal distortion constants have been determined.

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THE TORSIONAL SPECTRUM OF THE PARTIALLY DEUTERATED SPECIES OF METHANOL CALCULATED FROM A MULTIDIMENSIONAL AB INITIO POTENTIAL

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The first spectroscopic investigations of the partially deuterated species of methanol, CH_2DOH and CD_2HOH, have shown that these species display a dense torsional spectrum[a] difficult to assign. With a view toward understanding these spectra, a theoretical calculation of their rotation-torsion energy levels has been undertaken aided by *ab initio* calculations. This calculation accounts for the complicated torsion-rotation interaction displayed by these molecules and is based on the following features:

- The kinetic energy part of the Hamiltonian is calculated numerically taking into account all 12 internal degrees of freedom of the molecules. The angle of internal rotation is treated as an active coordinate.[b]
- The Schrödinger equation for the internal rotation is solved using Gaussian quadrature.[c]
- Internal degrees of freedom corresponding to the other small amplitude motions are treated using the harmonic approximation, for each value of the internal angle of rotation corresponding to the DVR grid.[d]
- The potential energy function of the molecule is obtained using *ab initio* calculations.

After making some reasonable assumptions for the dipole moment function, the last step of the calculation involves evaluating the intensity of the rotation-torsion transitions. In the paper we hope to be able to show plots of room-temperature absorption spectra.

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[d]Lauvergnat, Nauts, Justum and Chapuisat, *J. Chem. Phys.* **114,** 6592 (2001).

ANALYSIS OF THE HIGH RESOLUTION INFRARED SPECTRUM OF MONODEUTERATED ETHYLENE OXIDE BETWEEN 850-950 cm^{-1}

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Monodeuterated ethylene oxide C_2H_3DO or monodeuterooxirane, an asymmetric top, is an excellent example of a simple chiral molecule. The infrared spectrum of singly monodeuterated ethylene oxide has been recorded at an instrumental resolution (1/MOPD) of 0.001 cm^{-1} with the Bruker IFS 120 HR prototype in Zurich. The spectrum has been analysed in the region 850-950 cm^{-1}. Molecular constants for the ground and ν_8 (CH_2 twist, $\nu_c = 896.0$ cm^{-1}) states have been determined through an analysis of approximately 800 rovibrational transitions. Our results will be discussed in relation to isotopic chirality and parity violation as well as in relation to fluoroxirane [ab].

[a]H. Hollenstein, D. Luckhaus, J. Pochert, M. Quack and G. Seyfang, *Angew. Chemie*, **109**, 136-140 (1997).

[b]R. Berger, M. Quack, and J. Stohner, *Angew. Chemie*, **113**, 1716-1719 (2001).

ANALYSIS OF SOME COMBINATION AND OVERTONE INFRARED ABSORPTION BANDS OF $^{32}S^{16}O_3$

ALFONS WEBER, *National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A. and National Science Foundation, Arlington, VA 22230, U.S.A*; **ARTHUR MAKI**, *15012, 24th Ave., S.E., Mill Creek, WA 98012, U.S.A*; **T. A. BLAKE, S. W. SHARPE, AND R. L. SAMS**, *Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352, U.S.A*; **J. FRIEH, J. BARBER, T. MASIELLO, AND J. W. NIBLER**, *Department of Chemistry, Oregon State University, Corvallis, OR 97332-4003, U.S.A*

Several new infrared absorption bands for $^{32}S^{16}O_3$ have been measured and analyzed. The principal bands observed were $\nu_1 + \nu_2$ (at 1561 cm^{-1}), $\nu_1 + \nu_4$ (at 1594 cm^{-1}), $\nu_3 + \nu_4$ (at 1918 cm^{-1}), and $3\nu_3$ (at 4136 cm^{-1}). Except for the overtone band, these bands are very complicated because of the Coriolis coupling between ν_2 and ν_4, the Fermi resonance between ν_1 and $2\nu_4$, the Fermi resonance between ν_1 and $2\nu_2$, ordinary l-type resonance that couples levels that differ by 2 in the k and l quantum numbers, and the vibrational l-type resonance between the A_1' and A_2' levels of $\nu_3 + \nu_4$. Unraveling the complex pattern of these bands required a systematic approach to the understanding of the various interactions. Good estimates of as many constants as possible were necessary to begin the assignments and the fit of the measurements. Only in the case of the $3\nu_3$ band is the spectrum quite straight forward. The 003^10^0 state is only slightly perturbed by the 003^30^0 state through the l-type resonance constant, q_3, but that perturbation allowed us to obtain a reliable estimate of the separation of the two states.

In order to analyze the $\nu_1 + \nu_2$ and $\nu_1 + \nu_4$ bands, earlier work had shown that it was necessary to include the effects of the nearby states $3\nu_4$, $\nu_2 + 2\nu_4$, $2\nu_2 + \nu_4$, and $3\nu_2$. This was helped by the strong mixing of the different levels so that transitions to all states were observed with the exception of the $3\nu_2$ state. For the analysis we had to estimate the constants for that state by extrapolation from the already measured ν_2 and $2\nu_2$ states.

To help in our analysis of the $\nu_3 + \nu_4$ vibrational state, which occurs as three sub-states (E', A_1', and A_2'), we not only observed the allowed transitions from the ground state $(001^11^1)^2E' - (000^00^0)A_1'$, near 1918 cm^{-1}, but we also observed the hot band transitions, $(001^11^1)^2E' - (000^01^1)^1E'$, $(001^11^1)^0A_2' - (000^01^1)^1E'$, and $(001^11^1)^0A_1' - (000^01^1)^1E'$, accompanying the ν_3 band near 1390 cm^{-1}. Aside from the usual small vibrational changes in the various constants, the most important new constant that resulted from this fit is the vibrational l-type resonance constant, r_{34}, which was 1.75 cm^{-1}.

Invited Lectures G

Tuesday, September 9, 14:00

Chairman : L. S. ROTHMAN

NEW CHALLENGES IN ATMOSPHERIC SPECTROSCOPY AFTER THE MIPAS EXPERIMENT *(45 min.)*

BRUNO CARLI, *IFAC-CNR, via Panciatichi 64 - 50127 Firenze, Italy*

MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) is operating on board of the ENVISAT satellite since March 2002 and is acquiring for the first time high spectral resolution middle infrared emission spectra of the Earth atmosphere from space with a limb view. Full resolution spectra (0.025 cm-1) are acquired continuously at a rate of one spectrum every 7 seconds. A good accuracy has been reached in the spectroscopic data that are used for the profile retrieval of the target-species (O3, H2O, CH4, HNO3, N2O and NO2), but the large statistic of the measurements as well as the wide altitude range that is explored (from 6 to 68 km, with an extension to 100 km for some special modes) are making significant some effects that are often neglected, such as NLTE and lineshape distortions. A very good frequency accuracy is attained by MIPAS and an interesting new challenge may be posed by the exploitation of this information for the measurement of the speed of stratospheric winds.

MOLECULES IN ASTROPHYSICS: THE NEED FOR HIGH-RESOLUTION SPECTROSCOPY *(45 min.)*

EWINE F. VAN DISHOECK, *Leiden Observatory, P.O. Box 9513, 2300 RA Leiden, The Netherlands, ewine@strw.leidenuniv.nl*

More than 120 different molecules have been detected in interstellar space, most of them thanks to high-resolution spectroscopy at optical, infrared and millimeter wavelengths. In this talk, an overview will be given of recent discoveries of molecules, both in the gas and in the solid state, using new observational facilities in space (e.g., the *Infrared Space Observatory*, the *Far-Ultraviolet Space Explorer* and the *Submillimeter Wave Astronomical Satellite*) as well as on the ground. These include the detection of CO_2, CH_3, and C_6H_6 at infrared wavelengths, and SiC_3, SiCN, AlNC and more complex organic species at submillimeter wavelengths. In addition, huge deuterium fractionation effects are found, as evidenced by the detections of H_2D^+, D_2CO and ND_3. The results will be discussed in the context of the gas-phase and gas-grain processes occurring at low temperatures and densities. In addition, the use of molecules to trace the formation of new stars and planetary systems deep inside the dark molecular clouds is illustrated. The prospects for future facilities such as the *Atacama Large Millimeter Array*, the *Herschel Space Observatory* and the *James Webb Space Telescope* (the successor of the Hubble Space Telescope) will be discussed and the need for further high-resolution laboratory spectroscopy will be emphasized.

Poster Session H

Tuesday, September 9, 16:00

AMAT MILLS Award Applicant

REAL TIME DETECTION OF ETHYLENE IN AUTOMOBILE EXHAUSTS AND CIGARETTE SMOKE

M. T. MCCULLOCH, E. L. NORMAND, G. DUXBURY and N. LANGFORD, *Department of Physics, John Anderson Building, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, UK*

We have developed a pulsed quantum cascade laser spectrometer which uses a long duration top hat profile current pulse to produce a laser pulse which has an almost linear frequency down chirp. The spectrometer comprises a DFB QCL operating at a wavelength of 10.26 μm, excited by current pulses of up to 300 ns at repetition rates of up to 50 kHz. The output from the QCL passes through an astigmatic Herriott cell with an effective path length of up to approximately 100 m. The detection system following the cell comprises a fast photovoltaic HgCdTe detector, 1 GHz bandwidth amplifier and fast digitiser, and has an overall bandwidth of 500 MHz. The transform limited resolution is approximately 0.14 cm^{-1}. We will show that this spectrometer is able to detect the very weak carbon dioxide and water lines which lie within the laser chirp range, 974.5 to 972 cm^{-1}, and also to detect ethylene in automobile exhausts and in cigarette smoke.

AMAT MILLS Award Applicant

GLOBAL ANALYSIS OF NEW FT EMISSION SPECTRA OF THE C_2 SWAN SYSTEM

A. TANABASHI, T. HIRAO and T. AMANO, *Institute for Astrophysics and Planetary Sciences, Ibaraki University, Mito 310-8512, Japan*; **P. F. BERNATH**, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

From the dawn of spectroscopy, because it is important in astrophysics and it is a ubiquitous species in combustion and discharge systems of various hydrocarbons, the C_2 Swan system ($d^3\Pi_g - a^3\Pi_u$) has been subject to critical scrutiny. Therefore the general notion is that everything about it is under control.

However, it was found[a] that the transition wavenumbers for the (6,8) and (5,7) bands obtained by dye laser absorption technique did not agree with the well established literature values by Phillips and Davis[b]. In addition, we identified the (7,9) band that had never been identified before.

In the present study, emission spectra of C_2 covering the range from 14000 to 24000 cm^{-1} were re-recorded at University of Waterloo with Bruker IFS 120HR spectrometer by using microwave discharge in a mixture of a few tens mTorr of acetylene and about 2 Torr of argon buffer.

Several vibrational sequences of the Swan system were identified in the spectra and a total of 35 bands with $v' = 0$ to 10 and $v'' = 0$ to 9 were analyzed. The transition wavenumbers and the assignments for relatively low-v bands were found to agree with the Phillips and Davis compilation. On the other hand, for the higher vibrational bands (higher than around $v' = 4$), the line assignments have been found in many cases to disagree with tabulated literature values: a similar situation encountered in our previous laser investigation. Severely affected frequency regions turned out to be the regions of heavy line congestion and of overlapped bands.

We performed a global fit by including the transition wavenumbers of these bands together with those of our previous work. The rotational, spin-orbit, spin-spin, centrifugal distortion, Λ-doubling constants and the term values for each vibrational level were determined.

[a] A. Tanabashi and T. Amano, *J. Mol. Spectrosc.* **215**, 285-294 (2002).

[b] J.G. Phillips and S.P. Davis, "*The Berkeley Analysis of Molecular Spectra, Vol.2. The Swan System of the C_2 Molecule and the Spectrum of the HgH Molecule.*" Univ. of California Press, Berkeley (1968).

From these values, the equilibrium constants were derived for the upper and lower electronic states. These constants and newly determined transition wavenumbers should prove to be useful in astronomical observations as well as in monitoring reaction dynamics of combustion and discharge systems.

AMAT MILLS Award Applicant

STUDY OF THE LOW-ENERGY STRUCTURE OF SOME ASTROPHYSICAL SPECIES BY FOURIER-TRANSFORM SPECTROSCOPY

O. PIRALI, M. VERVLOET, *CNRS, Laboratoire de Photophysique Moléculaire, Université Paris-Sud, Bât. 350, 91405 Orsay Cedex, France*

FIRST (Far InfraRed Space Telescope) and ALMA (Atacama Large Millimeter Array) are future instruments which will be used to study galaxies, star formation, interstellar medium, clouds ... These instruments will record spectra of such astrophysical objects in the far-infrared (FIR) spectral region (55-500 μm).

Laboratory measurements are therefore necessary to complete the spectroscopic knowledge of astrophysically important molecules in this spectral region. We have recorded, under high resolution, gas-phase emission and absorption Fourier-Transform spectra of several astrophysical species in the FIR region.

Thermal emission spectra of hot small molecules (NH_3, HCN, H_2O and its isotopomers) have been recorded as well as spectra of radicals (NH_2, NH, OH) using different excitation sources. FIR emission spectroscopy (between 50 and 800 cm^{-1}) of Polycyclic Aromatic Hydrocarbons (PAHs) has also been performed. We have detected the low frequency bending vibrations of the aromatic rings which are the fingerprints of the PAHs molecules. The absorption spectrum of Naphtalene at room temperature, in the same spectral range, leads to resolve the P, Q and R branches of these vibrational transitions.

Preliminary results will be presented and discussed.

AMAT MILLS Award Applicant

STUDY OF THE ROTATIONAL SPECTRA OF $(CH_3)_3SnCl$ and $(CH_3)_2SiH\text{-}Sn(CH_3)_3$

MELANIE SCHNELL, DEIKE BANSER, JENS-UWE GRABOW,
Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstr. 3-3A, D-30167 Hannover, Germany

Until now only little is known about the barrier to internal rotation of methyl groups at tin atoms. Additionally, the geometries of many small tin containing species like dimethylsilyl-trimethylstannane $(CH_3)_2SiH\text{-}Sn(CH_3)_3$ cannot be determined using x-ray diffraction since it is often not possible to crystallize them. Furthermore, there are only very few spectroscopic studies investigating the bonding situation in tin containing molecules.

We have measured the microwave rotational spectra of trimethyl tinchloride $(CH_3)_3SnCl$ and $(CH_3)_2SiH\text{-}Sn(CH_3)_3$ between 3 GHz and 24 GHz using a pulsed molecular beam Fourier transform microwave spectrometer with coaxially orientated beam resonator arrangement (COBRA). The spectra exhibit rather dense line patterns due to internal rotation of the multiple methyl tops, quadrupole coupling of the chlorine atom and the large number of isotopic species.

AMAT MILLS Award Applicant

EXTREME ULTRAVIOLET LASER EXCITATION OF ISOTOPIC MOLECULAR NITROGEN

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The atmospherically important first dipole-allowed electronic transitions in molecular nitrogen access strongly mixed Rydberg and valence states of $^1\Sigma_u^+$ and $^1\Pi_u$ (singlet ungerade) symmetry. Interacting $^3\Pi_u$ states cause predissociation of the singlet ungerade states. This predissociation is a vital process in the photochemistries of the terrestrial and other nitrogen-rich planetary atmospheres. An accurate understanding of the N_2 predissociation mechanisms is required but is, at present, lacking.

We have studied the Rydberg-valence mixing of the singlet ungerade states of the isotopomers $^{15}N_2$ and $^{14}N^{15}N$ experimentally using XUV+UV two-photon ionization spectroscopy.[a] An ultra-high resolution XUV laser (bandwidth 250 MHz FWHM) was employed and resolving powers of up to 10^7 were achieved. A rotational analysis was performed, which yielded new molecular constants and accurate isotope shifts. For $^{15}N_2$ and $^{14}N^{15}N$, the band origins were calculated using the Fourier Grid Hamiltonian method in which the Hamiltonian is diagonalized on a DVR grid and the calculated band origins are in good agreement with the observed values.

Furthermore, we present new isotopic predissociation lifetimes obtained from linebroadening measurements performed in Amsterdam and from direct time-domain pump probe experiments using the Lund picosecond XUV laser. The lifetimes are found to be strongly isotope dependent. In addition, several new transitions were observed into triplet states and several local singlet-triplet interactions were analyzed.

[a] J.P. Sprengers, W. Ubachs, K.G.H. Baldwin, B.R. Lewis, and W.-Ü L. Tchang-Brillet, J. Chem. Phys. in press (2003).

All this new data, i.e. molecular constants, isotope shifts, isotopic predissociation lifetimes and singlet-triplet interactions are key inputs in a realistic predissociation model for N_2, which is currently being developed. This research has been supported within the Molecular Atmospheric Physics (MAP) program of the Netherlands Foundation for Research of Matter (FOM). e-mail: arjan@nat.vu.nl

AMAT MILLS Award Applicant

THE ROTATIONAL SPECTRUM OF CHLOROMETHANOL, A POSSIBLE CHLORINE RESERVOIR SPECIES

DEIKE BANSER, MELANIE SCHNELL, JENS-UWE GRABOW, *Institut für Physikalische Chemie, Universität Hannover, Callinstr. 3-3A, D-30167 Hannover, Germany*

Methyl hypochlorite (CH_3OCl) is known to play an important role as chlorine reservoir during the radical reduction of the atmospheric ozone. The isomeric chloromethanol is about 43 kcal/mol lower in energy than the hypochlorite and is formed by similar reaction pathways. Thus it is most likely that this molecule, too, is of importance for radical reactions of chlorine species in the atmosphere.

Microwave spectra of methyl hypochlorite were measured already in the sixties. To obtain experimental rotational data of the chloromethanol, too, the substance was produced in an electrical discharge of dichloromethane and methanol in neon as carrier gas and detected by time-of-flight (TOF) mass spectrometry. A Fourier transform microwave (FT-MW) spectrometer with coaxially oriented beam-resonator arrangement (COBRA) was used to record its rotational spectrum in the range of 10-24 GHz.

AMAT MILLS Award Applicant

MODIFIED DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY SYSTEM USING NEURAL NETWORKS AND COMPUTER SIMULATION

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Differential Optical Absorption Spectroscopy (DOAS) is a popular and powerful technique for monitoring atmospheric trace species in air pollution studies. The strength of this technique lies in the absence of wall loses, good specificity, and the potential for real-time measurements, specially it is well suited for detection of air pollutants in the range of ppb or better. A generalized Beer-Lambert equation which is a basis for DOAS technique can be written as [a]:

$$I(\lambda) = I_0(\lambda) exp[-L \sum \sigma_i'(\lambda) C_i] exp[-L(\sum \sigma_{i0}(\lambda) C_i) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda)] A(\lambda) \quad (1)$$

where $I_0(\lambda)$ denotes the initial intensity of the radiation source, $I(\lambda)$ is the intensity of the radiation after it passes through a layer of thickness L, C_i's are the concentration of the species to be found, σ_i' (σ_{i0})is the rapidly (slowly) part of the absorption cross section at wavelength λ, $\varepsilon_R(\lambda)$ and $\varepsilon_M(\lambda)$ are the Rayleigh extinction coefficient and Mie extinction coefficient, respectively. In the usual and conventional DOAS system, the final result output of the system are species concentrations which are usually obtained by curve fitting of the right hand side of Eq.(1).

In this work, various novel modifications on a DOAS system have been applied in order to enhance the system accuracy which is influenced by a series of temporal errors varying in experimental conditions.

These modifications have been accomplished both in software and hardware parts of the system.

A main source of the error accumulating in the final results is the temporal fluctuation of the source. To surmount this type of difficulties, the usual and conventional repeated calibration is tedious and time consuming. In this work, a computer-controlled shutter which can switch between the radiation source, which usually a Xe lamp, and the signal passed through the air has been designed. This hardware part can allow one to measure the intensity of the Xe lamp when commencing the new data collection each time necessary. Therefore, one does not need to live with the original calibration data during the

whole period of the experiment, however, one can collect the calibration data at any time needed. This procedure will eventually allow the experimenter to collect the more precise and qualified spectroscopic data.

From software point of view, an Artificial Neural Networks was trained using some collected computer simulated data. In these computer simulations, factors such as temporal fluctuation of Xe lamp, the resolution of CCD and the interference caused by different absorptive species existing in the air were considered. Now the trained Neural Networks can be utilized to get the real experimental absorption spectra of air as an input and delivers the concentrations of the various constituents as an output.

This procedure is totally based on the Neural Networks technique and the usual curve fitting of the data will be completely absent. In this respect, the number of the error sources which are usually blocks the collection of precise and reliable data will be remarkably reduced.

(1) W. Sigrist (editor) *Air Monitoring by Spectroscopic Techniques*, Chap 2. by U. Platt, Chemical Analysis Series, Vol. 127

AMAT MILLS Award Applicant

THE DETECTION OF THE ELECTRONIC SPECTRUM OF $FeCl_2$ IN THE GAS PHASE

STEPHEN H. ASHWORTH, *School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, NR4 7TJ, United Kingdom*; **PHILIP J. HODGES and JOHN M. BROWN**, *Department of Physical and Theoretical Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom*

A system of bands arising from the $FeCl_2$ radical has been recorded at high resolution by laser excitation spectroscopy around 288nm. This work confirms earlier observations at low resolution by DeKock and Gruen[a]. The molecule was formed in a high-temperature reaction between HCl and iron metal; the sample was cooled to a rotational temperature of about 10K in a subsequent free-jet expansion. In preliminary work[b], the carrier of the spectrum was identified from excited state vibrational progressions with an interval of about 200 cm^{-1} (assigned to two quanta of the bending vibration) and from fragmentary rotational analysis. These assignments have been confirmed by further work which includes extensive rotational analysis and a study by dispersed fluorescence; the latter reveals long progressions in the symmetric stretching vibration (353 cm^{-1}).

[a]C.W. DeKock and D.M. Gruen, *J. Chem. Phys.* 44, 4378 (1966).
[b]S.H. Ashworth, P.J. Hodges and J.M. Brown, *Phys.Chem.Chem.Phys.* 4, 5923 (2002).

NEW SPECTROSCOPIC DATA OF CHLOROFLUOROCARBONS AND HYDROCHLOROFLUOROCARBONS IN SUPPORT OF THE ANALYSIS OF ATMOSPHERIC DATA, OBTAINED BY HIGH RESOLUTION INFRARED SPECTROSCOPY

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Chlorofluorocarbons are playing an important role in atmospheric chemistry. Due to their chemical stability the CFCs accumulate in the stratosphere, where their photolysis is producing highly reactive chlorine atoms, which initiate a series of reactions converting ozone into oxygen. Infrared monitoring of these compounds, which are responsible for the stratospheric ozone depletion and contribute significantly to the global warming process is important for the conservation of the protective ozone layer and for studying changes in the global climate. Novel experimental techniques have been developed for obtaining fundamental spectroscopic parameters [a], necessary for interpretation of solar transmission spectra. High resolution spectra, using tunable diode lasers and supersonic slit-jet expansions have been obtained and analyzed for the most important CFCs [b,c] and HCFCs. The molecular parameters obtained by state-of-the-art spectroscopic techniques can be used to produce atmospheric spectra falling within the infra red atmospheric windows (8-12 micron) yielding an excellent agreement with laboratory spectra recorded under specific conditions (mixing ratio, temperature, pressure). The advantage of this approach is that spectra can be generated for a large variety of CFCs and HCFCs (depending on the spectroscopic data available for each compound) for any reasonable temperature, pressure and mixing ratio. Some spectra of CCl_3F (CFC-11) [d,e] and CH_3CF_2Cl (HCFC-142b) [f,g] are shown to demon-

strate the power of the diode-laser slit-jet technique.

(1) M.Snels, in Recent Res.Devel.Mol.Spectroscopy, 2002, ISBN 81-7895-026-X, Transworld Research Network, Kerala, India, 1-23.

(2) M. Snels and G. D'Amico, *J. Mol. Spectrosc.* **209** (2001) 1.

(3) M. Snels and G. D'Amico, H. Hollenstein, and M. Quack, *Phys.Chem.Chem.Phys.* **4** (2002) 1531-1536.

(4) M. Snels, A. Beil, H. Hollenstein, M. Quack, U. Schmitt, and F. D'Amato , *J.Chem.Phys.* **103** (1995) 8846.

(5) M. Snels, G. D'Amico, L. Piccarreta, H. Hollenstein, and M. Quack, *J. Mol. Spectrosc.* **205** (2001) 102.

(6) M. Snels and G. D'Amico, *Eur. Phys. J. D* **21** (2002) 137-142.

(7) G. D'Amico and M. Snels, *J. Mol. Spectrosc.* **217** (2003) 72-78.

THEORETICAL CALCULATION OF CONTINUUM ATMOSPHERIC ABSORPTION IN THE MILLIMETER AND FAR-INFRARED REGIONS

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In addition to absorption by discrete spectral lines of molecular species present in the atmosphere, there are also important continuum absorptions due to pairs of colliding molecules. The most important continua are due to $H_2O - H_2O$ (the self-continuum), $H_2O - N_2$ (the foreign continuum), and the collision-induced absorption (the dry continuum) by $N_2 - N_2$, $N_2 - O_2$, and $O_2 - O_2$ pairs. We will present some recent theoretical results and show comparisons with laboratory and atmospheric data.

LINE STRENGTHS AND HALF-WIDTHS OF N_2O AND CO_2 BANDS IN THE 2100–3800 CM^{-1} REGION AT ATMOSPHERIC TEMPERATURES

M.FUKABORI, T.AOKI, *Meteorological Research Institute, 1-1 Nagamine, Tsukuba, Ibaraki 3 05-0052 Japan*; **T.WATANABE,** *Toray Research Center Inc., 3-3-7 Sonoyama, Otsu, Shiga 520-8567 Ja pan*

The Improved Limb Atmospheric Spectrometer-II (ILAS-II) is a solar occultati on sensor to monitor the vertical profiles of O_3 and O_3-relate d species in the stratosphere with infrared and visible grating spectrometers. ILAS-II observes the transmittance of the solar spectra with three infrared channels which cover the 6.21–11.76 μm (CH.1), 3.0–5.7μm (CH.2), a nd 12.78–12.85μm (CH.3) spectral regions. In the spectral region of CH.2, there are important absorption bands of N_2O and CH_4. In addition, the very strong ν_3-fundamental band of CO_2 exists. In order to retrieve the vertical profiles of these gases, accurate absorpti on line parameters of CO_2 as well as those of N_2O and CH_4 are required. The main purpose of this study is to determine the accurate absorption line parameters such as the line strength, the half-width, and their temperature dependence of the infrared bands of CO_2 and N_2O required in th e data analysis of ILAS–II.

All the spectra were measured with a high-resolution Fourier transform spect rometer (Bruker IFS 120HR) at atmospheric temperatures. We used the temperature variable absorption cell with the path length of 1 cm. The sample temperature was measured with a thermocouple and the variation of the temperature was kept within 1K during the measurements. Sample pressures were measured with an MKS Baratron pressure gauge. A nonlinear least-squares fitting technique was used to determine the line s trengths as well as N_2- and O_2-broadened half-widths. The squared transition dipole moments and Herman-Wallis factors were also de termined using the weighted least-squares method.

The line strengths and half-widths of the ν_3 and $2\nu_1$ bands of N_2O and of the ν_3, $\nu_1+\nu_3$, and $2\nu_2+\nu_3$ bands of CO_2 were determined at 180K, 240K, and 296K. The measured line strengths of these bands agreed with the values of the HIT RAN databases within the experimental errors. The squared transition dipole moments of these bands at room temperature wer e in good agreement with the values at low temperatures within a few percent except high J lines. N_2- and O_2-broadened half-widths obtained in this study agreed well with the recent high-resolution experiments for both N_2O and CO $_2$. The temperature dependence of the half-width was determined assuming the pow er-law is valid. The exponent of the power-law for each line was determined with the weighted

least-squares method. The exponents of N_2- and O_2-broadened half-widths showed the d ependence on the rotational quantum number.

FAR INFRARED COMPENSATION EFFECT IN THE ATMOSPHERE

FERENC M. MISKOLCZI, *SAIC ASM, 1 Enterprise Pkwy., STE 300, Hampton VA 23666, USA*; **MARTIN G. MLYNCZAK**, *NASA LARC, 21 Langley Blvd.,Mail Stop 420, Hampton VA 23681-2199, USA*

The transmitted and emitted part of the clear-sky outgoing longwave radiation, OLR, were computed on a global scale temperature and water vapor profile set. The results of the LBL simulation showed, that in the far infrared the meridional variation of the OLR is unexpectedly small, and it does not reflect the large pole-ward decrease in the surface and atmospheric temperatures. It is also shown, that the far infrared normalized upward atmospheric emittance increases pole-ward partly compensating the decrease in the surface temperature. This phenomenon is the direct consequence of the downward shift of the peak of the weighting functions in the strongly absorbing far infrared H_2O rotational bands. The lack of an equator to pole gradient in the far infrared part of the OLR has been verified by satellite (ERBE) observations.

MILLENIUM HITRAN COMPILATION

L.S. ROTHMAN, D. JACQUEMART, and K. CHANCE,
Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA

The current edition of the HITRAN molecular absorption compilation[a] has been made available on an anonymous ftp-site located at the Harvard-Smithsonian Center for Astrophysics

ftp://cfa-ftp.Harvard.edu/pub/HITRAN

The compilation consists of five main folders: the traditional line-by-line parameter database; IR cross-sections; UV cross-sections and line-by-line parameters; aerosol refractive indices; and tables of globally applicable quantities (partition sums, isotopic abundances, molecular masses, etc), algorithms (for line-coupling corrections), and references to parameters and cross-sections. There is also a high-temperature analog of HITRAN called HITEMP. Some updates or corrections have been posted since the official release of the archival data in the ftp-site. These improvements are given in the public HITRAN web-site

http://cfa-www.Harvard.edu/HITRAN

and will be incorporated into the next edition.

Collaborations with many research teams throughout the world have enabled great improvements in providing more accurate parameters, extended spectral coverage, and documentation. The improvements not only will provide increased capabilities for atmospheric transmittance/radiance calculations and remote sensing, but also will allow access and analytical tools for related molecular databases. Besides the line-by-line absorption parameters, significant progress has been made for pressure-temperature sets of absorption cross-sections as well as increased tables of aerosol properties. A new edition of the HITRAN compilation is now in preparation.

[a]Rothman LS, Barbe A, Benner DC, Brown LR, Camy-Peyret C, Carleer MR, Chance KV, Clerbaux C, Dana V, Devi VM, Fayt A, Flaud JM, Gamache RR, Goldman A, Jacquemart D, Jucks KW, Lafferty WJ, Mandin JY, Massie ST, Nemtchinov V, Newnham D, Perrin A, Rinsland CP, Schroeder J, Smith K, Smith MAH, Tang K, Toth RA, Vander Auwera J, Varanasi P, Yoshino K, *JQSRT* **82**, in press (2003).

THE NEXT HITRAN EDITION: DESCRIPTION OF NEW PARAMETERS

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The current HITRAN compilation[a]

http://cfa-www.harvard.edu/HITRAN

consists of several components useful for radiative transfer calculation codes: high-resolution spectroscopic parameters of molecules in the gas phase, absorption cross-sections for molecules with very dense spectral features, aerosol refractive indices, ultraviolet line-by-line parameters and absorption cross-sections, and associated database management software. The line-by-line portion of the database contains spectroscopic parameters for thirty-eight molecules and their isotopologues suitable for calculating atmospheric transmittance and radiance properties.

The total length of a record (line transition) is 100 bytes, which has been adopted since the edition of 1986 and up to the current edition (i.e. edition of 2000 including updates through 2001). In the next edition, the number of parameters will be increased, and the record length will be 160. It should be noted that the parameters are independent quantities, valuable as input to various computer codes that simulate transmission or radiance in gaseous media. They have been chosen with respect to internationally accepted modeling schemes.

This poster describes the future format for the line-by-line portion of the HITRAN database, especially for a coherent vibrational and rotational quanta identification, as well as the description of the calculation of the Einstein-A coefficient (which replaces the weighted square of the transition moment) and the statistical weight of the upper and lower state of the transition.

[a]Rothman LS, Barbe A, Benner DC, Brown LR, Camy-Peyret C, Carleer MR, Chance KV, Clerbaux C, Dana V, Devi VM, Fayt A, Flaud JM, Gamache RR, Goldman A, Jacquemart D, Jucks KW, Lafferty WJ, Mandin JY, Massie ST, Nemtchinov V, Newnham D, Perrin A, Rinsland CP, Schroeder J, Smith K, Smith MAH, Tang K, Toth RA, Vander Auwera J, Varanasi P, Yoshino K, *JQSRT* **82**, in press (2003).

THE COLOGNE DATABASE FOR MOLECULAR SPECTROSCOPY, CDMS

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The unequivocal assignment of astronomically observed spectral lines depends decisively on the availability of appropriately precise laboratory data. One central part of the CDMS[a] is a catalog of (mostly) rotational transition frequencies of atomic and molecular species from the radio frequency to the far-infrared regions (i. e. frequencies up to 18 THz or wavelengths longer than 16.5 μm). Currently, the catalog contains almost 200 species of astrophysical, astrochemical, and planetary interest. It may be used as a guide in planning observations as well as a tool in analyzing observed spectral lines. The predictions are based on fits of critically reviewed experimental data. Emphasis is put on including newly characterized species and supplementing existing predictions towards higher frequencies. Particularly the latter aspect is of great relevance for upcoming missions such as the STRATOSPHERIC OBSERVATORY FOR INFRARED ASTRONOMY (SOFIA), the ATACAMA LARGE MILLIMETER ARRAY (ALMA) and the HERSCHEL SPACE OBSERVATORY. Recently added high frequency entries include C, CH, NH_2, OH^+, HCN, HNC, CO, H_2CO, CH_3OH, C_3, SO, HC_3N, and SO_2. Isotopomers and excited vibrational states are included whereever appropriate and available. Hence, the catalog is an important link between laboratory spectroscopy and astronomical observations. A search routine will be discussed briefly as will be the need for additional experimental data.

Other sections of the database list the molecules detected in interstellar space or circumstellar envelopes and provide the newest spectroscopic data obtained (partially) in Cologne. Recent changes to the database, links, and contact opportunities are also available. An additional section on fitting spectra gives information and examples to spectroscopy programs which are used in Cologne (currently limited to Herb Pickett's SPFIT and SPCAT).

The database is available online and free of charge through the KOSMA web-site
http://www.ph1.uni-koeln.de/ or directly *via* **http://www.cdms.de/**.

[a]H. S. P. Müller, S. Thorwirth, D. A. Roth, and G. Winnewisser, *Astron. Astrophys.* **370**, L49–L52 (2002).

NEW FEATURES OF THE MOGADOC DATABASE (MOLECULAR GASPHASE DOCUMENTATION)

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In order to facilitate the access to structural and related properties of free molecules, the Section for Spectra and Structure Documentation at the University of Ulm has compiled and critically evaluated for more than three decades literature in the field of microwave spectroscopy, molecular radioastronomy, and gas electron diffraction. On this basis the MOGADOC database (the acronym is standing for Molecular Gasphase Documentation) has been developped for IBM compatible personal computers.

MOGADOC enables the user to trace literature

- for microwave spectroscopy back to 1945,
- for molecular radioastronomy back to 1965,
- and for gasphase electron diffraction back to 1930.

The hierarchically constructed database contains now 29,300 bibliographic references for about 8,700 inorganic, organic, and organometallic compounds including numerical datasets for bond lengths and angles for about 5,100 compounds.

Recently a new WWW browser supported version has been developped. Its user-friendly graphical input interfaces enables text-based retrievals of bibliographic and structural information. Among the new features are extensive interactive thesaurus functions, fuzzy search and statistical functions[a].

Presently a structure and substructure retrieval tool, which utilizes the MOL format of the stored structural formulae, is being developped[b]. By means of an implemented Java-based structure editor the user can retrieve molecular structures and their fragments. Hereby one has the option to take into account or to ignore *cis-trans*-isomerism in ring systems or *(E)-(Z)*-isomerism at double bonds during the structure retrievals.

A demonstration of the MOGADOC database will be presented. Additional information is given through the web-site **http://www.chemie.uni-ulm.de/strudo/mogadoc/index.html**.

The project has been supported by the Dr. Barbara Mez-Starck Foundation.

[a] J. Vogt and N. Vogt, *Struct. Chem.* **14** (2003) 137-141.

[b] J. Vogt, N. Vogt, and R. Kramer, *J. Chem. Inform. Comput. Sci.* **43** (2003) 357-361.

STARK SPECTROSCOPY OF THE ETHYLENE MOLECULE : TENSORIAL FORMALISM FOR SPECTRUM SIMULATIONS

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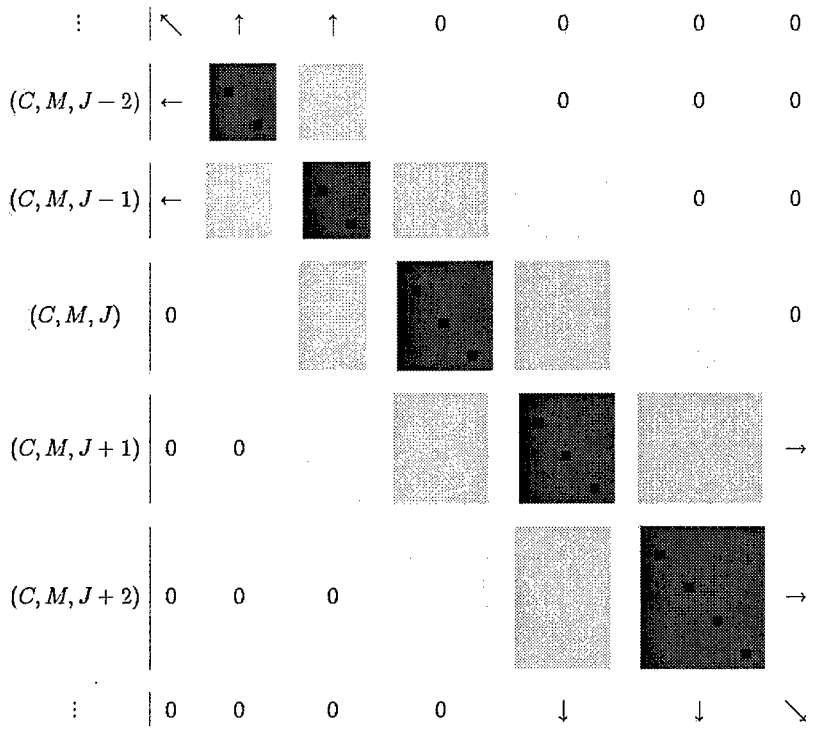
In a recent paper[a], we have already presented a tensorial formalism adapted to the case of D_{2h} asymmetric tops such as C_2H_4. It is part of an extension of the Dijon methods to symmetric and asymmetric tops like in our recent works performed on XY_5 (C_{4v})[b,c] and XY_2Z_2 (C_{2v})[d] molecules. These theoretical works have been used to develop the D_{2h}TDS program suite[e], in the aim of studying any rovibrational band or polyad of X_2Y_4 (D_{2h}) molecule.

We now intend to study the ethylene molecule in an electric field[f]. So we propose a model of the Stark effect. It is based on previous applications for XY_4[g] and XY_6[h] molecules. We give the expression of matrix elements of the Stark Hamiltonian. The figure below shows a schematic representation of the Stark matrix.

[a]W. Raballand, M. Rotger, V. Boudon and M. Loëte, *J. Mol. Spectrosc.*, **217**, 239-248, (2003).
[b]M. Rotger, V. Boudon and M. Loëte, *J. Mol. Spectrosc.* **200**, 123-130 (2000).
[c]M. Rotger, V. Boudon and M. Loëte, *J. Mol. Spectrosc.* **200**, 131-137 (2000).
[d]M. Rotger, V. Boudon and M. Loëte, *J. Mol. Spectrosc.* **216**, 297-307 (2002).
[e]Ch. Wenger, W. Raballand, M Rotger and V. Boudon, *J. Quant. Spectrosc. Radiat. Transfer*, in preparation.
[f]Yit-Tsong-Chen and T. Oka, *J. Chem. Phys.* **88**, 5282-90 (1988).
[g]M.-P. Coquard, Thèse d'État, Dijon (1994).
[h]N. Cheblal, M. Loëte and V. Boudon, *J. Mol. Spectrosc.* **197**, 222-231 (1999).


⋮
↖
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$(C, M, J-2)$
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$(C, M, J+2)$
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D_{2h} TOP DATA SYSTEM (D_{2h}TDS) SOFTWARE FOR SPECTRUM SIMULATION OF X_2Y_4 ASYMMETRIC MOLECULES

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The D_{2h}TDS (D_{2h} *Top Data System*) program suite[a] has been developed in the aim of studying any rovibrational band or polyad of X_2Y_4 (D_{2h}) asymmetric top molecules. It is based on the same principles as similar programs from our group already released for various molecular symmetries (T_d[b], O_h[c], C_{4v}[d], C_{2v}[e]). We work in the $O(3) \supset D_{2h}$ chain and this choice has consequences on the way used to specify the input parameters of the programs for Hamiltonian and transition moment calculations. In a previous paper[f], we have already described our tensorial formalism adapted to this case.

This suite consists in a series of FORTRAN programs called by a script. The whole package will be soon accessible through ftp (user anonymous) at `jupiter.u-bourgogne.fr` or through the World Wide Web at

`http://www.u-bourgogne.fr/LPUB/d2hTDS.html`

Two examples concerning the ν_{12} and ν_2 bands of the C_2H_4 molecule are presented. The figure below shows an overview of the experimental and simulated spectra for the ν_{12} band. The experimental spectrum has been recorded in Brussels by J. Vander Auwera.

[a]Ch. Wenger, W. Raballand, M Rotger and V. Boudon, *J. Quant. Spectrosc. Radiat. Transfer*, in preparation.

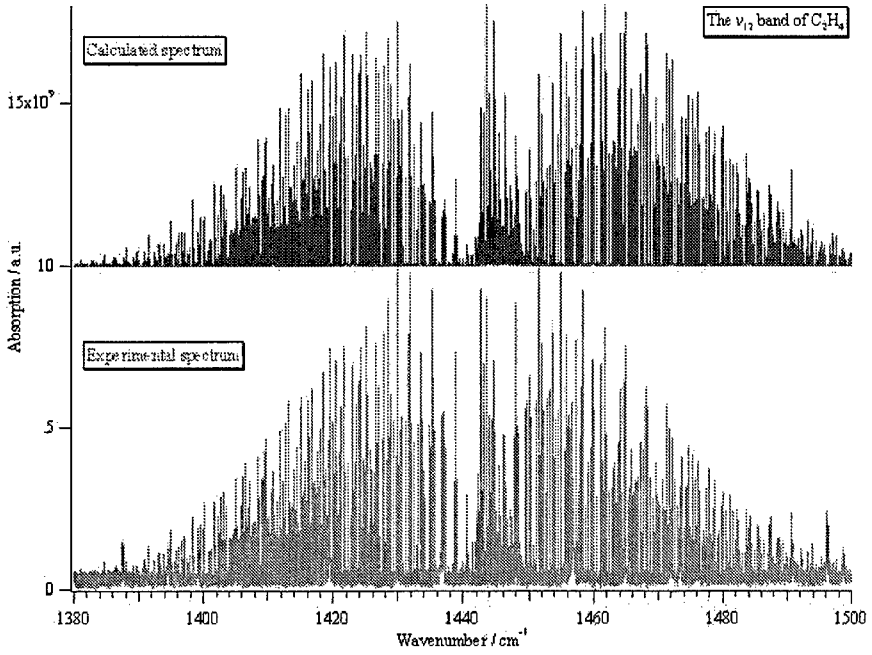
[b]Ch. Wenger and J.-P. Champion, *J. Quant. Spectrosc. Radiat. Transfer* **59**, 471–480, (1998).

[c]Ch. Wenger, V. Boudon, J.-P. Champion and G. Pierre, *J. Quant. Spectrosc. Radiat. Transfer* **66**,
1-16, (2000).

[d]Ch. Wenger, M. Rotger and V. Boudon, *J. Quant. Spectrosc. Radiat. Transfer* **74**, 621-636, (2002).

[e]Ch. Wenger, M. Rotger and V. Boudon, *J. Quant. Spectrosc. Radiat. Transfer*, in preparation.

[f]W. Raballand, M. Rotger, V. Boudon and M. Loëte, *J. Mol. Spectrosc.*, **217**, 239-248, (2003).


The ν_{12} band of C_2H_4
Calculated spectrum
Experimental spectrum
15x10⁵
10
5
0
Absorption / a.u.
1380
1400
1420
1440
1460
1480
1500
Wavenumber / cm⁻¹

CDSD-1000, THE HIGH-TEMPERATURE CARBON DIOXIDE SPECTROSCOPIC DATABANK AND INFORMATION SYSTEM

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We present a high-temperature version, CDSD-1000, of the Carbon Dioxide Spectroscopic Databank and the associated information system on the spectroscopy of carbon dioxide molecule. The databank contains the line parameters (positions, intensities, air- and self-broadened halfwidths and coefficients of temperature dependence of air-broadened halfwidths) of the four most abundant isotopic species of the carbon dioxide molecule. The reference temperature is $T_{ref} = 1000K$ and the intensity cutoff is $I_{cut} = 10^{-27} cm^{-1}/(molecule\ cm^{-2})$. More than 3 million lines covering the 260-8310 cm^{-1}, 418-2454 cm^{-1}, 394-4662 cm^{-1}, and 429-2846 cm^{-1} spectral ranges for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$, and $^{12}C^{16}O^{17}O$, respectively, are included in CDSD-1000. The databank has been generated within the framework of the method of effective operators and based on the global fittings of spectroscopic parameters (parameters of the effective Hamiltomians and effective dipole moment operators) to observed data collected from the literature. Line-by-line simulations of several low and medium resolution high-temperature ($T = 800 - 3000K$) spectra have been performed in order to validate the databank. Comparisons of CDSD-1000 with other high-temperature databanks HITEMP, HITELOR, and EM2C are also given. CDSD-1000 is able to reproduce observed spectra in a more satisfactory way than the high-resolution databank HITEMP for temperatures higher than $1000K$. The databank is useful for studying high-temperature radiative properties of CO_2. The CDSD-1000 is freely available at

`ftp://ftp.iao.ru/pub/CDSD-1000/`

An Internet accessible information system on the spectroscopy of carbon dioxide molecule based on CDSD databank has been elaborated. Its Internet address is `http://cdsd.iao.ru/`

This system allows users to calculate absorption coefficients, absorption, transmittance, radiance in wide ranges of temperature and pressure for defined

isotopic abundance and path length. This system also allows for modeling of spectra recorded with different kinds of spectrometers at different resolutions.

SELF-BROADENING COEFFICIENTS IN THE ν_4 BAND OF CH_4 BY DIODE-LASER SPECTROSCOPY

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Knowledge of spectroscopic line parameters of methane such as N_2- or O_2-collisional broadening coefficients[a] is very important for atmospheric applications. For their precise determination, it is necessary to take into account the self-broadening contribution and consequently to know precisely the corresponding coefficients.

With our diode-laser spectrometer[b], we have measured self-broadening coefficients of lines of the P-, Q- and R- branches in the ν_4 fundamental band of CH_4 at room temperature, with J values ranging between 0 and 12.

As the ν_4 band leads to a very strong absorption, to measure the self-broadening widths, we used an absorption cell with a small pathlength ranging between 4 and 17 mm and with pressures between 10 and 57 mbar. Each line under study, ranging from 1253 to 1368 cm^{-1}, was recorded at 4 different pressures.

For the determination of self-broadening parameters, we fitted to the experimental lineshape two theoretical line profiles: The Voigt profile taking into account Doppler and collisional broadenings, and the hard collision model developed by Rautian and Sobel'man incorporating Dicke narrowing. In all cases, the baseline was adjusted using a polynomial function. Small instrumental distortions were taken into account through an effective Doppler halfwidth obtained by comparing the line profile recorded at very low pressure to a Gaussian profile.

* Postdoctoral researcher with F.N.R.S., Belgium

[a]M. Lepère, A. Valentin, A. Henry, C. Camy-Peyret, G. Blanquet, J.C. Populaire, and A.W. Mantz, Spectrochim. Acta Part A **58**, 2413-2419 (2002).

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TEST OF THEORETICAL LINESHAPES FITTED TO EXPERIMENTAL PROFILES FOR CH_3D LINES BROADENED BY Xe

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J.-P. BOUANICH, *Laboratoire de Photophysique Moléculaire, CNRS, Université de Paris-Sud, Bâtiment 350, F-91405 Orsay cedex, France*

The well known Voigt model is often used to determine the line parameters. However, systematic discrepancies between this and the experimental profiles can be observed. Firstly, at small or moderate pressure, velocity-changing collisions take place and lead to a collisional narrowing of the Doppler profile. Considering this effect, we have used the hard collision model (HC) developed by Rautian and Sobel'man and the soft collision model (SC) of Galatry. Moreover, the speed dependence of the collisional cross-section must be taken into account, especially for larger pressures. This is realized by considering for the pressure broadening profile a weighted sum of lorentzian functions instead of a single lorentzian function. Taken into account the speed dependence effect (SD) in the Voigt and Rautian profiles, we have obtained respectively the V+SD and HC+SD models.

The lines of the light CH_3D molecule are relatively well isolated, which permits us to compare the fits of different theoretical lineshapes without perturbations from the wings of neighboring lines. Since the xenon mass is much greater than the CH_3D mass, the line parameters depend strongly on the velocity of the active molecule. For each line studied, we have fitted different theoretical lineshapes to the experimental profiles obtained using a diode-laser spectrometer at four mixing pressures between 60 and 170 mbar. Then, we have determined the Xe-broadening coefficients for 6 lines $\left({}^{Q}P(7,4),{}^{Q}R(3,2),{}^{Q}R(6,4),{}^{Q}R(10,2),{}^{Q}R(10,7),{}^{Q}R(12,4)\right)$ in the ν_3 band of CH_3D at room temperature. These coefficients are also calculated on the basis of the semi-classical model of Robert and Bonamy, assuming that CH_3D behaves like a linear molecule and considering the atom-atom Lennard-Jones potential for CH_3D-Xe interactions.

* Postdoctoral Researcher with F.N.R.S., Belgium

DIODE-LASER MEASUREMENTS OF SELF-BROADENING COEFFICIENTS IN ETHYLENE AT ROOM AND LOW TEMPERATURES

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Ethylene found as a trace constituent in the atmospheres of the outer planets[a] and of Titan[b] is formed by photo-dissociation of methane in the stratosphere of these planets. Therefore, knowledge of accurate spectral parameters, especially the self-broadening of C_2H_4 lines, is required for investigation of these atmospheres. We have recently measured N_2- and H_2-broadening coefficients[cd] in the ν_7 band of C_2H_4. However, to our knowledge, the self-broadening has only been measured at room temperature for one transition ($12_{0,12} \leftarrow 12_{1,12}$) in the ν_7 band[e] and another transition ($20_{11,10} \leftarrow 19_{10,9}$) in the ν_{10} band[f].

This report presents measurements of self-broadening coefficients for 17 transitions at 298 K and 18 transitions at 174 K, using a tunable diode-laser spectrometer and a low temperature cell. The collisional widths have been obtained by fitting the individual profile of each line to Voigt, Rautian and speed-dependent Rautian profiles. The experimental and data reduction procedures are similar to those described previously for the study of $C_2H_4 - N_2$ and $C_2H_4 - H_2$ broadenings as well as $C_2H_2 - H_2$[g] broadenings at low temperature and they will be briefly presented in the following sections.

A calculation of broadening coefficients was performed on the basis of a simplified semiclassical model of interacting linear molecules, involving only

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[f] V. Morozhenko, T. Kostiuk, W.E. Blass, T. Hewagama, T.A. Livengood, J. Quant. Spectrosc. Radiat. Transfer **72**, 193-198 (2002).

[g] J.P. Bouanich, J. Walrand, G. Blanquet, J. Mol. Spectrosc. **216**, 266-270 (2002).

electrostatic contributions of the potential. Finally, the temperature dependence of broadening coefficients is deduced experimentally from our measurements at 298 and 174 K, and theoretically from the calculated results at the same temperatures.

* Postdoctoral Researcher with F.N.R.S., Belgium

ABSORPTION OSCILLATOR STRENGTHS OF $^{12}C^{16}O$ and $^{13}C^{16}O$ IN THE VUV

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S. FEDERMAN, Y. SHEFFER [b], *Dept. of Physics & Astronomy, University of Toledo*

CO, the second most abundant interstellar molecule, is observed in absorption at ultraviolet wavelengths with the Far Ultraviolet Spectroscopic Explorer (FUSE) in the 900-1200 Å range. Interpretation of the spectra in terms of column density, temperature and turbulent line width requires the capability of precisely simulating the spectra using laboratory data including rotational line wavelengths, oscillator strengths and predissociation line widths.

Oscillator strengths for 6 strong absorption bands involving high Rydberg states, in the 956-1076 Å range for $^{12}C^{16}O$ and $^{13}C^{16}O$, have been measured using as a background source the SU5 high resolution beam line at the Super-ACO Synchrotron (Orsay France) with a resolution of 33000. An absorption cell of 54 mm in length was isolated from the monochromator and the electron storage ring by differential pumping and the pressure was maintained constant in the cell. Due to the use of a differentially pumped cell, the measured CO pressure has to be corrected to determine the CO column density. The procedure used has been validated by using as a standard the 3pπE-X(0-0) band oscillator strength recently measured by Federman et al in a closed cell. The absorption spectra were analyzed with a simulation fitting technique. The synthetic spectra were based on tabulated spectroscopic data. Each synthetic spectrum is adjusted to match the experimental spectrum in a nonlinear least squares fitting procedure with the band oscillator strength, the rotational excitation temperature of the ground state, the line width (instrumental and predissociation) and the wavelength offset as free parameters.

For the 3 overlapping bands, namely 4pπ-X(0-0), 3dπ-X (1-0) and 4pσ-X(0-0), the use of the simulation fitting technique allows us to fit each contribution separately. The fit is limited to the non overlapping P branch of the 4pσ-X(0-0) band, then to the R and Q branches for 4pπ-X(0-0) band and finally to the P and Q branches of the 3dπ-X(1-0) band. The results obtained with this separation procedure are in accord with those obtained for the 4pπ-X(0-0 and 4pσ-X(0-0) bands by Yoshino et al who eliminate overlap by cooling at 20K. The present results provide in addition a reliable measurement of the predissociation lifetime.

NEW ANALYSIS OF THE ν_5 AND $2\nu_9$ BANDS OF HNO_3: LINE POSITIONS AND LINE INTENSITIES

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Nitric acid (HNO_3) plays an important role in the Earth's atmosphere as a reservoir molecule of NO_x species. It has a strong infrared signature at 11 μm which is one of the most commonly used for the infrared retrieval of HNO_3 in the atmosphere since this spectral region coincides with an atmospheric window. It is therefore essential to have the best possible spectral parameters in this spectral region. The main goal of this work was to get better line positions and intensities for the ν_5 and $2\nu_9$ cold bands located at 879.1088 and 896.4482 cm^{-1} respectively. This work was also motivated by theoretical considerations. Very strong resonances involve the $v=5^1$ and $v=9^2$ rotational levels. In addition the ν_9 mode (OH torsion) is a "large amplitude" motion, and the torsional splittings are easily observed in the mm/submm region for the rotational transitions in the $v=9^2$ and $v=5^1$ excited states [a,b]. Both effects are accounted for in the present work. As far as the experimental data are concerned, in addition to the data available in the literature [a,b,c] new high resolution FTS spectra recorded in Giessen and new centimeter measurements performed in Kiel were used.

[a]T. M. Goyette, L. C. Oesterling, D. T. Petkie, R. A. Booker, P. Helminger and F. De Lucia, J. Mol. Spectrosc. 175, 395 (1996)

[b]D. T. Petkie, T. M. Goyette, P. Helminger, H. M. Pickett and F. De Lucia, J. Mol. Spectrosc. 208, 121 (2001)

[c]R. A. Toth, L. R. Brown, and E. A. Cohen, J. Mol. Spectrosc. 218, 151 (2003)

ON COLLISION-INDUCED ABSORPTION IN PURE O_2, CO_2 AND $CO_2 - O_2$ MIXTURES

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The NIST high-pressure absorption cell coupled to a DA002 Fourier-transform spectrometer has been modified in order to extend the lower temperature range of the measurements. Measurements of collision-induced absorption (CIA) of pure O_2 and CO_2 as well as $CO_2 - O_2$ mixtures have been recorded from room temperature down to $-80°$ C. The spectra of compressed CO_2 in the $\nu_1 - 2\nu_2$ infrared inactive Fermi dyad region consist of two anharmonically-coupled bands. Each of these bands includes a featureless CIA band on top of which is superimposed a distinctive CO_2 dimer band. These dimer bands increase in intensity with decreasing temperature but surprisingly persist up to room temperature. Spectra of mixtures of CO_2 and O_2 have also been obtained. As CO_2 is added to pure O_2 in the absorption cell, the intensity of the O_2 fundamental band grows rapidly. At higher CO_2 concentrations, the band narrows and unresolved ro-vibrational structure appears at the center. Its appearance indicates that a fairly strongly bound $O_2 \cdots CO_2$ complex is formed. Attempts are presently underway to model the observed van der Waals complexes as well as the structureless CIA profiles. Binary absorption coefficients have been derived for all species studied at 0.25 cm^{-1} intervals over the range 1100 to 1800 cm^{-1}.

AN EXAMINATION OF THE ENERGY CORRECTED SUDDEN SCALING PROCEDURE FOR THE CALCULATION OF ROTATIONAL RELAXATION OF CO IN ARGON

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We present measurements of Raman line widths in the fundamental Q-branch of CO for mixtures with Ar at temperatures of 77, 195 and 300 K, recorded using an inverse Raman spectrometer. Starting from a recent ab-initio potential energy surface, theoretical values of Ar broadening coefficients for CO infrared and Raman lines (isotropic and anisotropic components) at temperatures in the range 77 to 1100 K are calculated via quantum-mechanical methods. The relative merits of the close coupling theoretical results over the coupled states results are underlined. Finally, a comparison of the calculated pressure broadening coefficients is made with the present experimental data as well as with recently available infrared data. There is general agreement between the calculated and measured values of the broadenings for all the temperatures probed. We conclude that the temperature dependence of the infrared and Raman broadening coefficients have been correctly determined theoretically and may be used to test a common temperature scaling law. These fully quantal close-coupling and coupled-states scattering calculations were also used to test, in a first step, a scaling procedure based on the energy corrected sudden approximation: given a set of basic cross sections $\sigma(j \rightarrow 0)$, is it possible to predict the entire $\sigma(j \rightarrow j')$ relaxation matrix ? In a second step, we have examined another question: the validity of an inversion procedure, based on the same approximation. Is it possible, starting from the knowledge of the diagonal elements $\sigma(j \rightarrow j)$, the collisional HWHM, that can be easily measured, to determine the basic cross-sections $\sigma(j \rightarrow 0)$? Then, using a high resolution Raman spectrometer, we recorded the Q-branch head of the fundamental band of CO in mixture with Ar at three temperatures, 87, 195 and 300 K, and total pressures up to 1.25 bar. Line-mixing effects in experimental Raman profiles are compared with theoretical predictions. Finally the close coupling results are also used to predict rotational relaxation times measured in free jets.

SIMULATION OF THE SHPOLSKII SPECTRUM IN THE FRAMEWORK OF THE SIMPLEST π-ELECTRONIC MODEL

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Using the π-electron approximation, R. Pariser first demonstrated the possibility of achieving a quantitative agreement between the calculations of polyacene spectra and the experiment in 1956 [a]. Since then, this model has been applied to numerous spectral calculations for organic molecules with the π-electronic system. A small modification of this model (to the coupled cluster first order approximation) and an accurate adjustment of semi-empirical elements guarantees the accuracy of $0.1eV$ or the lowest singlet and triplet levels of several conjugated hydrocarbons[b]. However, the treatment of the Shpolskii spectra of this type of molecule in the crystalline matrix needs accuracy of one or two orders higher. Nevertheless, for certain molecules, like kekulene, even without further adjustment of parameters it is possible to achieve a higher accuracy[c] and obtain correct positions (within $0.01eV$) of the lowest singlet ${}^1B_{2u}^-$ and triplet ${}^3B_{1u}^+$ levels of this molecule.

This allows one to consider some peculiarities of the quasi-linear Shpolskii spectra of kekulene, particularly the details of the host matrix's influence on the guest molecule at different sites. The experimentally observed linear dependence of the zero-field splitting parameters D and E on the site shift of the triplet level $\Delta\lambda$ [d] of type $\Delta E = -2.1 \times 10^{-5}\Delta\lambda$, is derived from the perturbation theory. Two possibilities are considered: the action of the solvent molecules on the outstanding kekulene $C = C$ bond and on the external anthracene-type atoms. In the first instance, the calculation leads to $\Delta E_{(calc)} = -2.7 \times 10^{-5}\Delta\lambda_{(calc)}$ while in the second, the same dependence appears with the one order lower coefficient. Thus, the mechanism of the host influence corresponds to the first possibility. The triplet shift and splitting parameters have been calculated within the same theoretical model. The host influence on E, D, and λ has been simulated by the variation of the resonance integral of the outstanding bond (in the first instance) and of the Coulomb integral of the outer atoms (in the second instance) that reduces the molecular symmetry from D_{6h} to D_{2h}.

An attempt is also made to describe the lattice action by means of the crystal Lorentz factors, using one oscillator approximate formula for the crystal

[a] R. Pariser, *J. Chem. Phys.* **24**, 250, (1956).

[b] M.M. Mestechkin *Density matrix method in the theory of molecules*, Naukova Dumka, Kiev, (1977), p.370; *Izv. Ac. Sci. USSR*, **47**, *Phys. Ser.*, 1314, (1983).

[c] M.M. Mestechkin, A.L. Wul'fov, *J. Str. Chem.* **26**, 182, (1985).

[d] D. Schweitzer, K.H. Hausser, H.Vogler, *Mol. Phys.* **46**, 1141, (1982).

frequency shift: $\Delta\omega/\omega = (1 - f^{1/2})/f^{1/2}$, where f is the local field factor at zero frequency.

INTERACTIONS IN SYMMETRIC TOP MOLECULES BETWEEN VIBRATIONAL POLYADS: ROTATIONAL AND ROVIBRATIONAL SPECTROSCOPY OF LOW-LYING STATES OF PROPYNE, $H_3C–C{\equiv}CH$

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A large body of very accurate (mostly 10–20 kHz) rotational transitions within the 10 μm tetrad of the strongly prolate symmetric rotor propyne had been recorded in order to analyze some weaker resonances.[a] The analysis, in particular for higher K transitions, indicated new problems: Interactions of members of the 10 μm tetrad ($v_5 = 1$; $v_9 = v_{10} = 1$; $v_{10} = 3$; and $v_8 = 1$) with those of the 15 μm dyad ($v_9 = 1$ and $v_{10} = 2$) and possibly with those of the 7.5 μm heptad ($v_9 = 2$; $v_5 = v_{10} = 1$; $v_9 = 1$ & $v_{10} = 2$; $v_{10} = 4$; $v_8 = v_{10} = 1$; $v_4 = 1$; and $v_7 = 1$).

More than 300 rotational transitions within $v_{10} = 1$ ($E_{\mathrm{vib}} = 330.9\ \mathrm{cm}^{-1}$) have been recorded with $J'' \leq 53$ and $-11 \leq K \cdot l_{10} \leq +16$ for a more systematic investigation into the lower excited vibrational states of propyne. Even the inclusion of many high order terms prevented the highest K transitions to be fit within experimental uncertainties, in particular those having $K \cdot l_{10} \leq 0$. Inclusion of ν_{10} IR transitions from a reanalysis of the spectrum that was used in the study of the 10 μm tetrad[a] confirmed these findings. It turned out that the first order energies of the $K \cdot l_{10} = -12$ levels coincide to within $1\ \mathrm{cm}^{-1}$ with those of the overtone $v_{10} = 2$, $K = 12$ of the $l_{10} = +2$ substate. A weaker Coriolis interaction occurs between $v_{10} = 1$, $K \cdot l_{10} = -11$ and $v_9 = 1$, $K \cdot l_9 = +10$.[b]

Meanwhile, the investigation of $v_{10} = 1$ has been completed, and those of $v_9 = 1$ and $v_{10} = 2$ have begun. High K rotational and rovibrational transitions of $v_{10} = 1$ could be identified and fit easily until their intensities were too low. Fermi-type interactions occur between the states $v_{10} = 2$ and 3 and between $v_9 = 1$ and $v_9 = v_{10} = 1$. Among the Coriolis resonances

[a] P. Pracna, G. Graner, J. Cosléou, J. Demaison, G. Wlodarczak, V.-M. Horneman, and M. Koivusaari, *J. Mol. Spectrosc.* **206**, 150–157 (2001); H. S. P. Müller, P. Pracna, *et al.*, unpublished.

[b] H. S. P. Müller, P. Pracna, and V.-M. Horneman, *J. Mol. Spectrosc.* **216**, 397–407 (2002).

identified, the one between $v_{10} = 2$, $K = 9$, $l_{10} = -2$ and $v_5 = 1$, $K = 8$ permitted intervibrational transitions to be detected in the submillimeter region. These interactions are expected to improve A, D_K, etc. for $v = 0$. Selected details of our ongoing analyses will be presented. In addition, the relevance of these types of interactions for other symmetric top molecules will be discussed.

METHOD OF CORRECTED GREEN FUNCTION FOR CALCULATING FREQUENCY-DEPENDENT CHARACTERISTICS OF ATOMS AND MOLECULES

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A novel method is outlined for semi-empirical and *ab initio* calculating frequency-dependent (dynamic) characteristics of atoms and molecules, such as dynamic polarizabilities and hyperpolarizabilities. The method is based on the Green function technique, primarily devloped for hydrogen atom and high-excited Rydberg states[a]. In the present work this technique is modified in order to extend it to low-excited and ground states. For this purpose the terms in the Green function relating to the ground and low-excited states are corrected using *ab initio* wave functions for these states. As an illustration, we dynamic polarizability is calculated for several atoms and diatomic molecules. It is shown that the accuracy of calculation remains rather high in a very broad frequency range.

[a]V.A.Davydkin, B.A.Zon, N.L.Manakov, L.P.Rapoport. JETP, **60**, 124, 1971.

HIGHLY EXCITED $(6)^1\Sigma_u^+$ AND $(7)^1\Pi_u$ STATES OF K_2 FROM POLARIZATION LABELLING SPECTROSCOPY AND AB INITIO CALCULATIONS

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Although the low-lying molecular states of the K_2 molecule are quite well known, few experiments have been devoted to highly excited states dissociating above the doubly excited limit K(4p)+K(4p). Potential energy curves (PECs) for such states might present not regular shapes including shelf, hump, double-well structures, at short and intermediate internuclear separations. In the present work experimental excitation spectra have been obtained in a spectral range extended farther to the ultraviolet. This enabled us to observe for the first time the $(7)^1\Pi_u$ state correlating adiabatically to K(4s)+K(6p) as well as to refine substantially the description of the $(6)^1\Sigma_u^+$ state correlating adiabatically to K(4s)+K(6s). Literature theoretical results about the electronic structure of K_2 are too restricted with respect to the energy range of the new spectra considered here. Then an extended theoretical investigation has been performed for the 98 states in the representation $^{1,3}\Lambda_{g,u}^{(+/-)}$ dissociating into limits up to K(4s)+K(5d), among which the two states under investigation. The IPA-PEC with a quite exotic shape has been determined for the state $(6)^1\Sigma_u^+$ as well as the RKR-PEC for the state $(7)^1\Pi_u$. Experimental data including spectroscopic constants will be presented and compared to our most recent theoretical predictions.

THEORETICAL SPIN-ORBIT STRUCTURE FOR THE ALKALI DIMER CATIONS K_2^+, Rb_2^+ AND Cs_2^+

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Advances in the knowledge of ultralow temperature gases have induced recently a new interest in alkali dimer cations M_2^+. This enlarges the usefulness of accurate theoretical data on the electronic structure of these species, which furthermore constitute basic data for investigations of collisions as well as photodissociation processes. While for these systems there exist theoretical results for states in the representation $^2\Lambda_{g,u}^{(+)}$, to the best of our knowledge their spin-orbit structure have not yet been investigated. Present work takes place in this scope with the aim to produce not yet available accurate data on K_2^+, Rb_2^+ and Cs_2^+. 58 molecular states in the representation $\Omega_{g,u}$ dissociating to limits up to $K^+ + K(6p^2P_J)$, 38 states $\Omega_{g,u}$ dissociating to limits up to $Rb^+ + Rb(7s^2S_{1/2})$ as well as 38 states $\Omega_{g,u}$ dissociating to limits up to $Cs^+ + Cs(8s^2S_{1/2})$ have been investigated. A synthesis of the main results will be presented.

POSITIONS AND INTENSITIES OF ^{18}O OZONE ENRICHED ISOTOPOMERS : THE 5 μm REGION REVISITED

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The 5 μm region is one of the infrared windows used for the molecules atmospheric trace gas retrieval. For ozone, it corresponds to the triad $2\nu_3$, $\nu_1+\nu_3$, $2\nu_1$ where $\nu_1+\nu_3$ is the strongest band. This region has been revisited using the Fourier Transform Spectrometer built in GSMA laboratory (Reims, France). Infrared ^{18}O ozone enriched isotopomers spectra have been recorded, and the positions and intensities of all the six isotopic species have been reinvestigated. The analysis were performed using the effective ro-vibrational Hamiltonian, considering the usual scheme of polyad of (002), (101), (200) interacting upper vibrational states. The $2\nu_3$ and $2\nu_1$ bands of the $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{18}O^{18}O^{16}O$ and $^{18}O^{16}O^{18}O$ isotopic species have been observed and completely assigned for the first time, leading to a knowledge of these species similar to those of the $^{16}O_3$ [a], [b] and $^{18}O_3$ [c] species. Hamiltonian parameters and transition moment parameters are presented.

[a] A. Barbe, J.-J. Plateaux, S. Bouzza, J.-M. Flaud, C. Camy-Peyret, *J. Quant. Radiat. Transfer*, 48, 599-610, (1992).

[b] A. Barbe, J.-J. Plateaux, S. Bouzza, O. Sulakshina, S.M. Mikhailenko, Vl.G. Tyuterev and S.A. Tashkun, *J. Quant. Radiat. Transfer*, 52, 341-355, (1994).

[c] A. Chichery, A. Barbe, Vl.G. Tyuterev, M.T. Bourgeois, *J. Molec. Spectrosc.*, 206, 1-13, (2001).

NEW ANALYSIS OF THE CORIOLIS-INTERACTING ν_2 AND ν_5 BANDS OF CH_3Br : LINE POSITIONS AND INTENSITIES

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Methyl bromide (CH_3Br) has been identified as one of the major sources of atmospheric bromine. Atmospheric methyl bromide originates from both natural (algae, phytoplankton) and anthropogenic sources (agricultural fumigant): the tropospheric mixing ratio of CH_3Br is 9-11 pptV in the Northern hemisphere and about 8 pptV in the Southern hemisphere, with an increase of about 0.15 pptV per year[a].

However, until present, no attempts have been made to determine atmospheric concentrations of CH_3Br using infrared spectroscopy. The purpose of the present study is to provide a complete prediction of line positions and intensities in the spectral region between 5-10 μm. Although the line positions in the region have been studied previously at medium spectral resolution (0.015 cm^{-1})[b], little is known about the line intensities. The absorption spectrum of the ν_2 and ν_5 bands of CH_3Br has been recorded at LPPM with a high-resolution Fourier-transform spectrometer (resolution of 0.004 cm^{-1}). More than 7500 transitions between 1240 and 1650 cm^{-1} were assigned for both isotopic species $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$, with K values up to 11 and J values up to 58. By taking into account the xy-Coriolis interaction between the two bands, the entire spectrum has been reproduced with a standard deviation of better than 7×10^{-4} cm^{-1}. We now plan a set of intensity measurements to be performed in the LADIR laboratory. The possibility of atmospheric detection of CH_3Br will be discussed.

[a]World Meteorological Organization (WMO),"Scientific Assessment if Ozone Depletion: 1998", Report 44, WMO Global Ozone Research And Monitoring Project, Chapter 2, Geneva, Switzerland, 1999.

[b]Anttila, R., C. Betrencourt-Stirnemann, and J. Dupre, The infrared bands ν_2 and ν_5 of CH_3Br with Coriolis interaction, J. Mol. Spectrosc., 100, 54, 1983.

DYNAMICAL STRUCTURE OF PEPTIDE MOLECULES USING FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATION: N-METHYLFORMAMIDE, N-ETHYLACETAMIDE

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The peptide bond is central to biological molecules; it may play a significant role in transferring information through living body. We have been investigating several molecules which contain one or two peptide bonds, by using Fourier transform microwave spectroscopy as a main tool. We focus special attention to intramolecular dynamics of large amplitude motions such as CH_3 internal rotations, because they might convey signals from one group to another in the molecule by exchanging knowledge on the respective conformation through the coupling between the two groups via the peptide bond.
The rotational spectrum of both the *trans* and *cis* forms of N-methylformamide (NMFA) using FTMW spectrometers at NIST and KAIT, in the frequency region from 4 to 118 GHz, with either Ne or Ar as a buffer gas in a reservoir nozzle maintained at about 50°C. We assigned the E state of both forms of NMFA using the sum rule and observed some forbidden transitions. The V_3 value of *trans* is 56.4 cm^{-1}, which is close to that of the Caminati's work[a]. This value is 4.5 times smaller than the value of *cis* form which was determined to be 279 cm^{-1}. We have found by an *ab initio* calculation MP2/6-31G** that the V_3 internal rotation in NMFA *trans* is accompanied by the N-H out-of-plane angle bending by as large as 13°.
All *a*-, *b*-, and *c*-type transitions of N-ethylacetamide (NEAA) were observed and assigned in the frequency region from 4 to 25 GHz. Each transition showed large $A-E$ splitting, which were ascribed to the internal rotation of the methyl group directly bonded to the peptide linkage, i.e. to CH_3 in the acetyl group. The analysis of the observed spectra led to the rotational constants, which were indicative of a *trans* – *ac* non-planar conformation of the heavy atom skeleton, and to the methyl internal-rotation potential barrier V_3 of 75.36 (5)

[a]A. C. Fantoni, W. Caminati, H. Hartwig, and W. Stahl, *J. Mol. Struct.* **512**, 305-307 (2002).

cm^{-1}, which was close to that of N-methylacetamide.

ROVIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF THE $v_2 = 1$, $v_5 = 1$, AND $v_3 = 2$ LEVELS OF $^{13}CH_3{}^{37}Cl$

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Fourier-transform IR spectra measured between 1235 and 1680 $cm^{-1}$and millimeter wave spectra recorded between 198 and 455 GHz of monoisotopic $^{13}CH_3{}^{37}Cl$ have been analyzed simultaneously, taking into account all Coriolis, α-resonance, and l-type interactions in the polyad of $v_2 = 1$, $v_5 = 1$, and $v_3 = 2$ levels. A particular coincidence of the two fundamental levels with the overtone level constitutes a strongly interacting, but fairly isolated polyad with several level crossings due to the α-resonance ($\Delta k = \pm 2, \Delta l = \mp 1$) and x-y Corilois interaction ($\Delta k = \pm 1, \Delta l = \pm 1$). The resonances with a $\Delta(k - l) = \pm 3$ selection rule for nonvanishing matrix elements generate perturbation-allowed transitions which are used for an accurate determination of the axial rotational and centrifugal distortion constants. We have assigned two series of perturbation-allowed transitions in the FTIR spectra which provide the information on the separation of the pairs of K = 4-7 and 5-8 levels in the vibrational ground state, enabling an accurate determination of the A_0 and D_K^0 constants.

THE PURE ROTATION SPECTRUM AND THE VIBRATIONAL FUNDAMENTALS OF $^{123}SbD_3$

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The infrared spectrum of the ^{123}Sb isotopomer of deuterated stibine, SbD_3, has been recorded in the regions between 460 and 530 cm^{-1} and between 1235 and 1470 cm^{-1} at a resolution of about 0.0024 and 0.0027 cm^{-1}, respectively, using a BRUKER 120 HR interferometer.

Rovibrational transitions belonging to the ν_2, ν_4 bending and ν_1, ν_3 stretching fundamental bands have been measured and assigned. The $\nu_1(A_1)$(symmetric Sb-D) and ν_3 (E)(antisymmetric Sb-D) stretchings are nearly degenerate, the band origins being at 1358.3 and 1362.2 cm^{-1}, respectively. A total of about 2500 rotation-vibration transitions have been assigned with J' and K' up to 22.

The band centers of the $\nu_2(A_1)$ and ν_4 (E) bendings are at 561.25 and 590.49 cm^{-1}, respectively. In this case a total of about 3600 rotation-vibration transitions have been assigned with J' and K' up to 24.

Strong perturbations due to rovibrational interactions have been observed both in bending and stretching bands. Splittins of the $K" = 3$ lines have been observed and several $\Delta(k-l) = \pm 3$ "perturbation allowed" transitions have been identified. Simultaneuos analyses of transitions belonging to ν_1/ν_3 and ν_2/ν_4 dyads have been performed. The theoretical model adopted for the simultaneous analysis of the two strongly interacting vibrational states included all the symmetry allowed rotation-vibration interaction terms up to the fourth order of approximation.

The far infrared spectrum of a sample containing both ^{121}Sb and ^{123}Sb isotopomers in natural abundance has been recorded in the 20 - 90 cm^{-1} region with a resolution of 0.0023 cm^{-1}. $\Delta J = +1$ pure rotation lines were assigned up to $J' = 30$. Far infrared data and ground state combination differences obtained from all the fundamental bands have been combined to yield significantly improved ground state constants including the k-dependent ones, C, D_K, H_K and the $\Delta k = \pm 3$ interaction constants, ϵ, ϵ_J , and ϵ_K.

HIGH RESOLUTION RO-VIBRATIONAL ANALYSIS OF VIBRATIONAL STATES OF A_2 SYMMETRY OF THE DIDEUTERATED METHANE CH_2D_2

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The spectroscopy of the deuterated methane isotopomers is of fundamental importance for understanding and improving full-dimensional potential energy and electric dipole hypersurfaces [1,2].

In the present contribution we report results of a high resolution analysis of the two A_2-states $(v_5 = 1, A_2)$ and $(v_7 = v_9 = 1, A_2)$ of CH_2D_2.The ro-vibrational structure of the $(v_7 = v_9 = 1, A_2)$ state was derived from the analysis of the two hot bands, $\nu_7 + \nu_9 - \nu_7$ and $\nu_7 + \nu_9 - \nu_9$, including states up to J=13.

The rovibrational energies of the$(v_5 = 1, A_2)$ state were obtained from the analysis of the two hot bands $\nu_5 + \nu_7 - \nu_5$ and $\nu_5 + \nu_9 - \nu_5$. In a first step we derived ro-vibrational energies of the $(v_5 = v_7 = 1, B_2)$ and $(v_5 = v_9 = 1, B_1)$ states from an analysis of the combination bands $\nu_5 + \nu_7$ and $\nu_5 + \nu_9$ located in the region 2300-2700 cm^{-1}. In order to extract the information on this two combination bands the complicated structure of this region had to be "cleaned" from absorption due to other bands such as $2\nu_9$, $\nu_3 + \nu_4$, and $\nu_3 + \nu_7$. In a second step the region of the two hot bands $\nu_5+\nu_7-\nu_5$, $\nu_5+\nu_9-\nu_5$ (1000-1400 cm$-$1) had to be "cleaned" from contributions due to the fundamentals ν_7, ν_9 and other hot bands.

We finally obtained ro-vibrational wavenumbers of the $(v_5 = 1, A_2)$ state, up to J=12, with an accuracy of 0.001-0.003 cm^{-1} which is an improvement by a factor of 30-40 in comparison to known Raman data [3].

The high resolution spectra were measured with the BOMEM FTIR spectrometer in Zürich, with a best apodized resolution of 0.004 cm^{-1}, using a long path cell with 42 m path length and sample pressures of 2 and 10 mbar.

1. H. Hollenstein, R. Marquardt, M. Quack, and M. Suhm, J. Chem.

Phys., **101**, 3588 - 3602 (1994).

2. R. Marquardt and M. Quack, J. Chem. Phys., **109**, 10628 - 10643 (1998).

3. J. C. Deroche, G Graner, J. Bendtsen, and S. Brodersen, J. Mol. Spectrosc., **62**, 68-79 (1976).

HIGH RESOLUTION SPECTRUM OF CH_2D_2: THE $2\nu_9$, $\nu_3+\nu_4$, $\nu_5+\nu_9$, $\nu_5+\nu_7$, AND $\nu_3+\nu_7$ BANDS

O. N. ULENIKOV, E. S. BEKHTEREVA, *Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk, 634050, Russia, and Institute of Atmospheric Optics SB RAN, Tomsk, 634055, Russia*; **H. HOLLENSTEIN, M. QUACK**, *Physical Chemistry, ETH-Zürich , CH-8093 Zürich, Switzerland*

The spectroscopy of the deuterated methane isotopomers is of fundamental importance for understanding and improving full-dimensional potential energy and electric dipole hypersurfaces [1,2].

High-resolution ($\Delta\tilde{\nu}$= 0.004 cm^{-1}, FWHM), FTIR spectra of CH_2D_2 in the region 2350 - 2650 cm^{-1} were recorded with the BOMEM DA002 spectrometer in Zurich, using a long path cell with the path length set to 42 m, and a sample pressure of 10 mbar.

Transitions were assigned to the five very weak first overtone and combination bands, $2\nu_9$, $\nu_3+\nu_4$, $\nu_5+\nu_9$, $\nu_5+\nu_7$, and $\nu_3+\nu_7$. These were then analyzed in details. Two bands, $\nu_5+\nu_7$, and $\nu_3+\nu_7$, have not been analyzed before. The three others bands were assigned earlier up to the states corresponding to $J_{max.}^{upper}$ = 9, 9, and 11 for the bands $2\nu_9$, $\nu_3+\nu_4$, and $\nu_5+\nu_9$, respectively, [3]. In our new analysis, we were, however, able to assign transitions up to $J_{max.}^{upper}$ = 18.

The analysis is also in progress, where all five bands are fitted with the Hamiltonian model which takes into account resonance interactions between all the vibrational levels. The *rms* deviation of the fit is about 0.003 cm^{-1} which is close to experimental uncertainties.

1. H. Hollenstein, R. Marquardt, M. Quack, and M. Suhm, J. Chem. Phys., **101**, 3588 - 3602 (1994).

2. R. Marquardt and M. Quack, J. Chem. Phys., **109**, 10628 - 10643 (1998).

3. O. N. Ulenikov, A. B. Malikova, G. Guelachvili, and M. Morillon-Chapey, J. Mol. Spectrosc., **159**, 422 - 436 (1993).

CALCULATION OF NEW LINELISTS FOR WATER ISOTOPOMERS AND ANALYSIS OF EXPERIMENTAL SPECTRA

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The new linelists for water isotopomers $H_2{}^{17}O$ and $H_2{}^{18}O$ have been calculated using the DVR3D program suite developed at UCL. The program suite calculates energy levels, wavefunctions and dipole transition moments for rotating and vibrating triatomic molecules.[a] In this study we have used the potential energy surface (PES) developed by Shirin *et al.*[b], which is more accurate than the one by Partridge and Schwenke[c] in the high frequency region. We have calculated the linelists for $H_2{}^{17}O$ and $H_2{}^{18}O$ up to J=10.

Using the new linelists, the isotopomer enriched spectra recorded by Chevillard *et al.*[d] have been reanalysed and further assignments were made. For $H_2{}^{18}O$ spectrum in 12400-14520 cm^{-1} region covering the $3\nu + \delta$ and 4ν polyads, 819 lines out of 927 are now assigned, improving on our previous result of 747.[e] We are also analysing the spectrum of $H_2{}^{18}O$ in 16570-17120 cm^{-1} region recorded at the Vrije Universiteit in Amsterdam using the cavity-ring-down spectroscopy with the new linelist. This spectrum samples the 5ν polyad and is the highest region for $H_2{}^{18}O$ to be studied. Previously it was impossible to make assignments in this region due to inaccuracy of theoretical calculations at high frequencies. The new linelist seems to agree very well with the experimental spectra, which means that our linelist is significantly more accurate than the previous results. We have so far assigned more than half of the lines and the final results of this analysis will be presented at the conference.

We would like to thank Prof. O. Naumenko for helpful discussions.

[a] J. Tennyson, M. A. Kostin, P. Barletta, G. J. Harris, J. Ramanlal, O. L. Polyansky, N. F. Zobov, *Computer Phys. Comm.* (submitted).

[b] S. V. Shirin, O. L. Polyansky, N. F. Zobov, P. Barletta, J. Tennyson, *J. Chem. Phys.*, **118**, 2124-2129 (2003).

[c] H. Partridge and D. W Schwenke, *J. Chem. Phys.*, **106**, 4618-4639 (1997).

[d] J. -P. Chevillard, J. -Y. Mandin, J. -M. Flaud, C. Camy-Peyret, *Can. J. Phys.*, **63**, 1112-1127 (1985).

[e] M. Tanaka, J. W. Brault, J. Tennyson, *J. Mol. Spec.*, **216**, 77-80 (2002).

Invited Lectures I

Wednesday, September 10, 9:00

Chairman : T. R. HUET

LASER SPECTROSCOPY OF ISOLATED DNA BASES AND BASE PAIRS: STRUCTURE AND PHOTOCHEMISTRY *(45 min.)*

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Intrinsic properties of isolated biomolecules and large parts of their energy landscape can be investigated by high resolution laser spectroscopy in molecular beams and directly compared to theory. Different tautomers and electronic states of Adenine as well as Adenine-Thymine and Adenine-Adenine base pairs and their methyl substituted derivatives are observed and assigned based on resonant two photon ionisation and IR-UV and UV-UV double resonance experiments in a supersonic jet. Expansion conditions were chosen to preferentially form small clusters. The IR-UV spectrum in the range of the NH stretch vibrations fits cluster structures with HNH$\cdots$O=C/N$\cdots$HN hydrogen bonding based on the comparison with the A and T monomer IR spectra and with ab initio calculated vibrational spectra of the most stable A-T isomers. The Watson-Crick A-T base pair is not the most stable base pair structure at different ab initio levels and its vibrational spectrum is not in agreement with the observed experimental spectrum. The Adeninedimer shows HNH$\cdots$N/N$\cdots$HN hydrogen bonding. 9-Methyladenine - adenine has a stacked structure and exhibits extremely efficient hydrogen transfer upon electronic excitation. Adenine shows H atom dissociation upon UV excitation as exhibited by 2+1-REMPI at 243 nm.

The results show that isolated AT and GC do not form the Watson-Crick structures. Probably the special orientation of the DNA backbone forces these structures. Experiments with basepairs substituted at the sugar position in the DNA are in preparation. The photochemical stability of the DNA bases and bases pairs and their mechanism of conversion of electronic excitation to the ground state is criticallly discussed based on our experimental results of hydrogen transfer and N-H photodissociation.

STRUCTURES AND DYNAMICAL BEHAVIORS OF LARGE MOLECULES OF BIOLOGICAL SIGNIFICANCE IN A SOLVENT-FREE ENVIRONMENT *(45 min.)*

W. LEO MEERTS, *Department of Molecular and Laser Physics, University of Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands*

The conformations of a molecule plays a crucial role in molecular recognition processes, which are the basis for all selective biochemical reactions. Even small biomolecules have a structure with several conformers of partly comparable energies. Nevertheless, under physiological conditions, generally only a few conformers show up. This is a surprising and important observation, because the reactivity and functionality of biologically active substances is governed by their structure.

Especially the interaction of those molecules with surrounding molecules most importantly water is determined by their structure. The controlled complexation by a small number of water molecules and the subsequent mapping of the conformational landscape after each solvation step should result in a deeper understanding of how and why biomolecules change their molecular shape when they are dipped into a water bowl.

High Resolution UV Laser spectroscopy[a,b] is an excellent tool to obtain detailed structural information on large molecules and their hydrogen bonded clusters. The experimental technique which allow us to obtain rotationally resolved Ultra Violet spectra with a resolution of typically 10 MHz will be discussed.

From these rotationally resolved spectra we can deduce not only the relevant structural information, but in addition the direction of the electric dipole moment from the intensities and the lifetimes of the electronically excited states from the line widths. The latter can be used to investigate radiative and nonradiative relaxation channels in these molecules.

Recently we have applied the method of Genetic Algorithm[c] in the analysis of these complex spectra. This has proven to be a very powerful tool which

[a]See for example: Internal rotation effects in the rotationally resolved $S_1(^1L_b) \leftarrow S_0$ origin bands of 3-methylindole and 5-methylindole. K. Remmers, E. Jalviste, I. Mistrik, G. Berden and W.L. Meerts. J. Chem. Phys. 108 (1998) 8436-8445.

[b]High resolution UV spectroscopy of phenol and the hydrogen bonded phenol-water cluster. G. Berden, W.L. Meerts, M. Schmitt and K. Kleinermanns. J. Chem. Phys. 104 (1996) 972-982

[c]Direct Determination of Molecular Constants from Rovibronic Spectra with Genetic Algorithms. J.A. Hageman, R. Wehrens, R. de Gelder, W.L. Meerts and L.M.C. Buydens. J. Chem. Phys. 113 (2000) 7955-7962.

can be used for routine like analyses but also turned out to be very valuable in an automatic assignment of entangled spectra.

Poster Session J

Wednesday, September 10, 11:00

PHOTOPHYSICS AND CONFORMATIONAL STRUCTURES OF BIOMOLECULES: ROTATIONAL BAND CONTOURS OF DNA BASE ADENINE AND AMINO ACID PHENYLALANINE

YONGHOON LEE, JIWON JUNG, and BONGSOO KIM,
Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejon 305-701, Korea

Rotational contours of DNA base adenine and amino acid phenylalanine have been obtained by resonant two-photon ionization (R2PI) in a pulsed molecular beam. As for the adenine, rotational contour spectra of three dominant vibronic bands at 36062, 36105, and 36248 cm^{-1} near the origin of the $\pi - \pi^*$ transition reveals the electronic structure of adenine responsible for its photophysical behavior induced by UV absorption. From the band contour analysis and a simple group theoretical consideration, we could identify the close-lying $\pi\pi^*$ and $n\pi^*$ states and their mixed vibronic level. As for the phenylalanine, six stable conformers have been experimentally observed in gas phase.[a] We obtained the rotational contour spectra of the $S_1 - S_0$ origin bands of six conformers and their low frequency vibrational bands. The observed rotational contours vary with conformation. In addition, the excited-state lifetimes of six conformers were measured by 2-color R2PI delaying the ionization laser pulse from the excitation one. Particularly, the conformer labelled as X in ref. 1 shows very short lifetime. From the observation of rotational contours and the measurement of lifetime it was found out that the electonic structure of phenylalanine is very sensitive to the interaction between the chromophore and the amino acid side chain.

[a]L. C. Snoek, E. G. Robertson, R. T. Kroemer, J. P. Simons, *Chem. Phys. Lett.* **321** 49-56 (2000).

HIGH-RESOLUTION INFRARED ABSORPTION SPECTRUM AND ANALYSIS OF THE $\nu_2 + \nu_4$ COMBINATION BAND OF SF_6

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N. LACOME, *LADIR, UMR CNRS 7075, Case 49, Université Paris 6, 4 Place Jussieu, F-75252 Paris Cedex 05, France*

SF_6 is now recognized as a pollutant that can contribute to the greenhouse effect[a]. However, the spectroscopic knowledge of this molecule, which is necessary for a correct remote sensing and monitoring in the Earth's atmosphere, is still very partial. In particular the hot bands in the strongly absorbing ν_3 region (near 948 cm^{-1}) have not been analyzed yet. Their knowledge implies the analysis of many vibrational levels and thus the spectroscopy of various fundamental, harmonic and combination bands.

Some progress in SF_6 spectroscopy have been made recently[b,c,d]. The present work is a new contribution to this topic, concerning the $\nu_2 + \nu_4$ combination band. The FTIR spectrum of this region has been recorded at room temperature with a resolution of 0.002 cm^{-1}. The data have been analyzed thanks to the HTDS software (`http://www.u-bourgogne.fr/LPUB/shTDS.html`)[e] developed in Dijon for XY_6 octahedral molecules. 759 lines could be assigned up to $J = 113$, and the standard deviation is 0.0022 cm^{-1}. The distance between the two vibrational sublevels with respective symmetry F_{1u} and F_{2u} is 0.348 cm^{-1}. The figure below shows a comparison between experimental and simulated spectra in the central part of the $\nu_2 + \nu_4$ band.

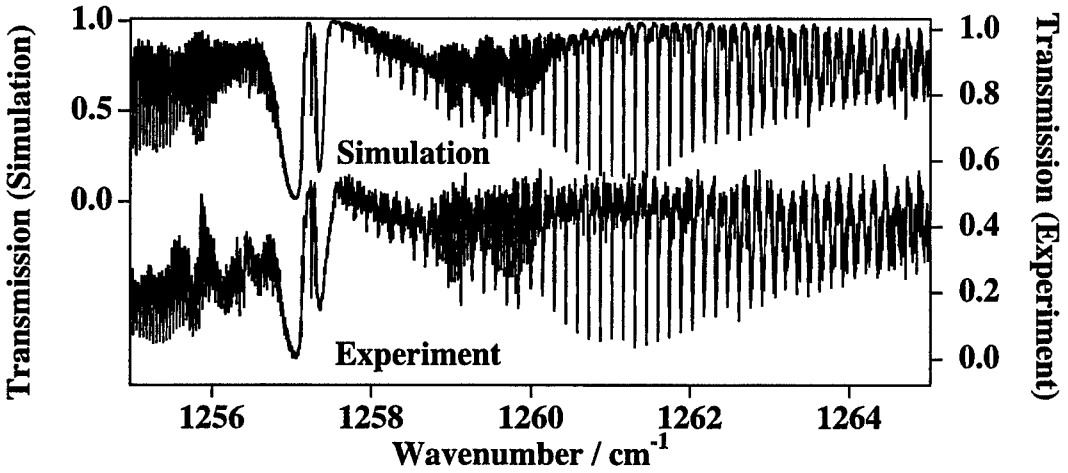
[a] L. Geller, J. Elkins, J. Lobert, A. Clarke, D. Hurst, J. Butler, and R. Myers, *Geophys. Res. Lett.*, **24**, 675–678 (1997).

[b] V. Boudon and G. Pierre, *Rovibrational Spectroscopy of Sulfur Hexafluoride: A Review*, in *Recent Research Development in Molecular Spectroscopy*, S. G. Pandalai Ed., vol. 1, pp. 25–55, Transworld Research Network (Trivandrum, India), 2002.

[c] V. Boudon and D. Bermejo, *J. Mol. Spectrosc.*, **213**, 139–144 (2002).

[d] R.R. Gamache, N. Lacome, G. Pierre and T. Gabard, *J. Mol. Struct.* **599**, 279–292 (2001)

[e] Ch. Wenger, V. Boudon, J.-P. Champion and G. Pierre, *J. Quant. Spectrosc. Radiat. Transfer*, **66**, 1–16 (2000).


Transmission (Simulation)
1.0
0.5
0.0
Simulation
Experiment
1.0
0.8
0.6
0.4
0.2
0.0
Transmission (Experiment)
1256
1258
1260
1262
1264
Wavenumber / cm-1

APPLICATION OF THE GENETIC ALGORITHM IN THE ANALYIS OF COMPLEX MOLECULAR SPECTRA

W. LEO MEERTS, *Department of Molecular and Laser Physics, University of Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands*; **MICHAEL SCHMITT**, *Institut für Physikalische Chemie I, Heinrich-Heine-Universität, Universitätsstrasse 26.43.02, D-40225 Düsseldorf, Germany*; **GERRIT. C. GROENENBOOM**, *Institute of Theoretical Chemistry, University of Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands*

It has been shown[a] that the Genetic Algorithm can be used in the assignment of high density spectra. Since the method does not require an initial assignment of quantum numbers to the individual transitions it can be of great help in the analysis of complex spectra with many (partly) overlapping lines. The major requirement for the success of the technique is that the theoretical model is capable to predict both the positions and intensities of the spectrum.

High resolution rotational resolved UV-laser spectra form in general a perfect class of spectra to be analyzed by the Genetic Algorithm using an asymmetric rotor Hamiltonian.

One of the major drawbacks for application was the relatively large amount of computing time needed to perform a convergence calculation using the Genetic Algorithm. We have greatly improved the various algorithms to obtain the evaluation function[a] which is used as a criterium for the quality of the fit. Together with a few other improvements on the computing process this has resulted in a reduction of the computing time by a factor of 10. It is now within the scope of modern PC's, even with a single processor, to perform a full Genetic Algorithm convergence on a complicated spectrum over lunchtime. This can be done without any prior assignments of transitions nor knowledge of the parameters.

We will show results on previously investigated spectra of ^{18}O substituted phenol[b] and results on the Ne-benzonitrile cluster not previously assigned in the conventional way.

[a]Direct Determination of Molecular Constants from Rovibronic Spectra with Genetic Algorithms. J.A. Hageman, R. Wehrens, R. de Gelder, W.L. Meerts and L.M.C. Buydens. J. Chem. Phys. 113 (2000) 7955-7962.

[b]The structure of phenol in the S_1-state determined by high resolution UV-spectroscopy. Ch. Ratzer, J. Küpper, D. Spangenberg and M. Schmitt. Chem. Phys. 283 (2002) 153

APPLICATION OF PATTERN RECOGNITION METHOD TO PEAK SEARCHING AND LINE ASSIGNMENT

L.N. SINITSA, O.V. NAUMENKO, A.M. PSHENICHNIKOV, A.P. SHCERBAKOV, *Institute of Atmospheric Optics, SB RAS, Tomsk, Russia, 634055*

An expert system for automatic peak searching and assignment of the complex vibrational-rotational spectra of molecules has been developed. System was used for automatic line search and determination of line parameters in spectra containing thousands of lines. Doppler, Lorentz and Voigt profiles are used as contour in fitting procedure. In practice, 20 steps of education were necessary before automatic line searching. Fourier transform spectrum of D_2O in 3200-4200 cm^{-1} was developed by the system. 4670 lines were found in the spectrum consisting 439000 spectral points, no one line seeing by scientist was not omitted by the system. An iteration approach is implemented in this system, in which employment of the exact combination rule is combined with determination of the spectroscopic constants by solving of the inverse problems and comparison of the calculated parameters of spectral lines with the corresponding measured values. In order to calculate the energy levels and the frequencies and intensities of lines, the Watson Hamiltonian, the Pade-Borel approximants, and generating functions are used. The system is based on the application of pattern-recognition algorithms. Recognition training makes it possible to obtain the required flexibility of the system and to use different methods of identification based on the application of combination rules both for the analysis of strong bands and for the assignment of weak single lines. The system developed can be used to analyze the spectra of the Cs and C2V molecules, as well as employ the calculated spectrum of a molecule of any type prepared in advance. This system was successfully used to identify spectra of the H_2O, D_2O, HDO,and H_2S molecules. The work is done in the frame of the RAS program "Optical spectroscopy and frequency standards"

HIGH-RESOLUTION SPECTROSCOPY OF FLUOROSTYRENE, 3-METHYLINDOLE AND THEIR NOBLE GAS AND WATER CLUSTERS

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High-resolution spectroscopy is a powerful tool for the investigation of the structure and dynamics of polyatomic molecules and clusters[a]. High-resolution spectra provide valuable information on the interaction between a polyatomic molecule and a noble gas atom or another molecule, thus elucidating the solvation processes which play a vital role in chemistry and biology and which are of both fundamental and practical importance for science and technology.

In our research we employ a high-resolution mass resolved resonance enhanced multiphoton ionization experiment. The combination of the theoretical methods for the simulation of the spectra of asymmetric rotors and the correlation automated rotational fitting (CARF) technique[b, c] is promising as a suitable approach for the analysis of congested rotational structure of UV spectra of the systems considered, and for this reason it is extensively used in our work. In a series of high-resolution experiments data for the rovibronic transitions in the 0_0^0 origin band of fluorostyrene and 3-methylindole were obtained and for their clusters with argon and water.

In the case of fluorostyrene the substitution of the fluorine atom in the styrene molecule causes the electron density shift within fluorostyrene thus giving rise to a dipole moment formation. On the basis of the measured spectra the rotational constants can be determined and the value of the dipole moment can be measured on the basis of the Stark splitting in the excited state[d]. Regarding the fluorostyrene-water cluster two possible positions of the water molecule with respect to the fluorostyrene plane are considered: in-plane and out-of-plane. Ab initio calculations show the energy of the in-plane configuration is less than that of the other configuration. The results of the CARF procedure applied to the measured spectrum will be a figure of merit for this assumption.

Indole is a molecule of biological importance and hence it has attracted

[a]K. Siglow, H. J. Neusser, *Chem. Rev.* **100**, 3921 (2000).
[b]R. M. Helm, H.-P. Vogel, H. J. Neusser, *Chem. Phys. Lett.* **270**, 285 (1997).
[c]R. M. Helm, H. J. Neusser, *S.S. Xantheas (ed.)*, 281 - 300, *Kluver* (2000).
[d]K. Siglow, H. J. Neusser, *J. Phys. Chem A* **105**, 7823 (2001).

the scientific interest in the recent years[e]. Another interesting molecule is 3-methylindole, which is a good prototype for the amino acid tryptophan whose fluorescence is very useful in the spectral probe of biological systems. We have measured the high-resolution UV spectrum of 3-methylindole and for the first time the high-resolution spectrum of the fluorostyrene-water cluster. This investigation aims at revealing its rovibrational structure in the excited state and it may cast light upon the solvation process of this molecule at molecular level, thus allowing some inferences about the solvation behaviour of the stated molecule in various chemical and biological structures to be made.

[e]R. M. Helm, M. Clara, Th. L. Grebner, and H. J. Neusser, *J. Phys. Chem. A* **102**, 3268 (1998).

RECENT DEVELOPMENTS IN THE LASER SPECTROSCOPY OF LANTHANIDE HALIDES

C. LINTON, M. J. DICK AND R. K. GHOSH, *Physics Department, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*

As part of a continuing investigation of the properties and structure of lanthanide molecules, a laser spectroscopic study of the lanthanide halides is presently in progress. High-resolution spectra are obtained via both Broida oven and laser ablation sources using a cw ring laser. At present, high-resolution spectra of several electronic transitions of Holmium monofluoride and Holmium and Dysprosium monochlorides have been obtained and others are being investigated. A global fit of the transitions has been completed for each molecule. The results and analysis of both rotational and hyperfine structure will be presented and discussed in terms of the electron configurations of the electronic states. In addition, work continues on constructing a map of the low-lying electronic states. The nature and energy of these states will be discussed for each molecule and compared and contrasted with calculations done via the Ligand Field Theory.

LABORATORY SPECTROSCOPY OF SMALL CARBON CLUSTERS

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Carbon containing molecules play a dominant role in interstellar chemistry. Small pure carbon chain molecules have been found as constituents in a variety of extrasolar sources, such as the tails of comets, shells of late type stars and in star forming regions of interstellar clouds. As pure carbon chains display no rotational spectrum, it is inevitable to look for the IR-active vibrational stretching modes and for low bending modes in the far-IR.

In our laboratory, the clusters are produced in an UV-laser ablation source and detected by a high resolution infrared diode laser spectrometer, leading to rotationally resolved spectra of asymmetric stretching modes. Chemical information (structure, etc.) as well as reference data for astrophysical observations can be derived. Up to now we were able to assign the linear forms of several pure carbon clusters. In order to control the conditions and to enhance the yield of cluster production a plasma monitoring system has been implemented. First tests as well as recent measurements will be presented.

STUDYING CLUSTERS OF ORGANIC MOLECULES WITH Ar AND H_2O USING MASS ANALYZED THRESHOLD IONIZATION

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The spectroscopic technique of Mass Analyzed Threshold Ionization (MATI) has been used for studying the vibrational spectra of organic molecular cations and their clusters with Ar and H_2O[a, b]. This method is based on the laser excitation of high lying long-lived Rydberg states 5 - 15 cm^{-1} below a selected ionization threshold. The excitation itself consists of two steps: in the first step the molecules are promoted from S_0 to some vibrational level of S_1; in the second step an excitation to high Rydberg states combined with a direct electric field ionization follows. Separating the Rydberg molecules from the promptly produced ions in a delayed pulsed field ionization scheme leads to state and energy selected ions which are mass analyzed in a time-of-flight (TOF) mass spectrometer. Because of the mass selectivity dissociation thresholds of the clusters can be measured when the ion internal energy is increased and a breakdown of the parent ion signal caused by dissociation is observed. Here we report the results from our experiments on hydrogen and van der Waals clusters of *trans*-1-Naphthol and p-Fluorotoluene. The hydrogen and the van der Waals bonds originate from the "weak" intermolecular interactions and play a significant role in a great variety of physical, chemical and biological phenomena like protein folding.

In the case of the hydrogen-bonded *trans*-1-Naphthol·H_2O cluster we investigate the influence of water molecules attached to the OH group of *trans*-1-Naphthol on the vibrational structure of the ionic ground state. We present MATI spectra for *trans*-1-Naphthol and *trans*-1-Naphthol·H_2O cluster via different intermediate states, displaying a rich variety of intra- and intermolecular vibrational bands. In addition we give values for the binding energies of the $OH\cdots OH_2$ in the neutral ground and cationic states of the cluster[c].

For the van der Waals bonded p-Fluorotoluene·Ar cluster we determine the binding energy of this complex in the ground cationic and neutral state, using 0_0^0 and $9b_0^1$ bands of S_0 to S_1 transition as a first step in the MATI experiment. We also observe a small shift for some bands in the MATI spectrum of the

[a] J. Braun, Th. Mehnert, H. J. Neusser, *Int. J. Mass Spectrom.*, **203**, 1 (2000).
[b] J. Braun,Th. L. Grebner, H. J. Neusser, *J. Phys. Chem.* A **102**, 3273 (1998).
[c] J. Braun, H. J. Neusser, *submitted for publication.*

parent and the daughter cations when exciting the cluster, which we conclude may be due to the influence of the Ar atom on the vibrational modes of the p-Fluorotoluene or to the excitation of bending intermolecular vibrations. Another interesting result from our experiments is the split profile of the 0_0^0 band in the p-Fluorotoluene$^{+\cdot}$Ar complex spectrum. Our conclusion for this splitting is the excitation of the bending intermolecular vibrations in the low excess energy region.

ON THE USE OF CLASSICAL TRAJECTORIES IN LINEWIDTHS CALCULATIONS

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Semiclassical linewidths models have been used for several decades to calculate the collisional broadening of spectral lines. The original model so-called ATC, used a straight line trajectory described with constant velocity and only long ranged intermolecular forces were taken into account. This model has been found accurate for highly polar molecules. In the RB model, the straight line has been replaced by a parabolic trajectory around the distance of closest approach and the molecular interactions included both long and short ranged forces. The latter ones were approximated by atom-atom (Lennard-Jones type)interactions between pairs of atoms added to electrostatic ones. This simple form of the potential leads to analytical expressions of the resonance functions. The RB model has proven its efficiency for a large variety of molecules and in a large range of temperatures. A further improvement has consisted in introducing an exact trajectory description and including any typ e of potential, the calculations being thus purely numerical. The consequences of these successive modifications on the line broadening calculations are carefully analyzed. Numerical tests are made on the CO molecule which is both infrared and Raman active, and for which a large number of linewidths data is available.

COLLISIONAL BROADENING OF C_2H_2 ABSORPTION LINES BY AN EXACT TRAJECTORY APPROACH

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Apart from simple molecules like nitrogen and oxygen, the planetary atmospheres consist of more complex polyatomics which are important in environment monitoring and/or astrophysical studies. One of such systems is acetylene (C_2H_2). In the Earth's atmosphere, C_2H_2 is mainly produced by anthropogenic sources and is destroyed by chemical reactions with OH and Cl^-. Its detection is therefore informative for better understanding of the ozone cycles as well as for the developement of pollutants transport models. Spectral lines of C_2H_2 have been equally observed in the atmospheres of Jupiter, Saturn and Titan. The exhausive study of this system, consequently, turns out to be equally important for complete understanding of the photodissociation processes occuring on these planets.

For the abovementioned atmospheric applications, a good knowledge of spectral line positions and pressure-broadening coefficients is required. From the experimental point of view, acetylene provides a good probe system since its spectrum is well resolved rotationally (great value of rotational constant) and is straightforward to analyse (linear molecule). A lot of experimental data have been obtained for various C_2H_2 absorption bands [1]. The theoretical interpretation of linewodths has been realisized [1] on the basis of two semiclassical impact approaches: the Anderson-Tsao-Curnutte theory [2,3] and the more elaborate Robert-Bonamy formalism [4]. The last approach was found [1] to be quite realistic to describe the C_2H_2 collisional linebroadening.

We present here a theoretical analysis of absorption linebroadening coefficients of C_2H_2 in the framework of Robert-Banamy approach but with another trajectory model. This model consists in using the exact solution of classical equations of motion governed by an isotropic potential [5]. Various anisotropic interaction models are tested: a simple potential composed of quadrupole-quadrupole term and of an anisotropic dispersion contribution [6] as well as a usual sum of quadrupole-quadrupole and atom-atom interactions. Our theoretical results compare favorably with both previous computations and experimental data available [1].

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PRECISE LINE STRENGTHS AND COLLISION BROADENING PARAMETERS FOR THE ν_3 BAND OF SO_2 DETERMINED BY DIFFERENCE FREQUENCY SPECTROSCOPY

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The strongest infrared absorption band of SO_2 is the ν_3 band located between 1300 and 1400 cm^{-1}. While the line center wavenumbers have been mapped with very high accuracy and are reported in HITRAN with 0.00001 cm^{-1} resolution, the accuracy of line strengths and collision broadening parameters is less than adequate. Previous publications [1,2] have reported line strengths which are typically 60% to 80% of the HITRAN values, and a significant quantum number dependence has been observed for the self broadening parameter, which is given in HITRAN as a common value of 0.4 cm^{-1}/atm for all lines. Using the difference frequency spectrometer described previously [2], we have conducted a systematic investigation of the quantum number dependence for the line paramenters over the entire Q- and P-band. For the line strength the results support previous conclusions, and deviations up to a factor of 2 are observed. For the collision broadening parameter we observe no systematic trend if J is varied for fixed K_a, whereas a decrease by up to a factor of two for fixed J and increasing K_a seems to be a general feature.

In [3] the spectrometer, which is based on mixing of radiation from diode lasers in $AgGaSe_2$, was used over a narrow wavenumber range around 1344 cm^{-1} for monitoring SO_2 released from wine. Here it is used over a signficantly wider region, thus confirming the potential of the difference frequency spectrometer for systematic high resolution spectroscopy. The main peak of the phase matching curve has a full half width of about 10 cm^{-1}, and can be shifted by another 10 cm^{-1} by angle tuning. A notable feature is the presence of 6 side lobes extending towards high frequencies with gradually decreasing power. With a peak power level of 10 nW at 1345 cm^{-1}, a power of 50 pW in the fifth side lobe still allows for observation of water lines in the lab air beyond 1400 cm^{-1}.

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THE $X^2A_1 - A^2B_2$ CONICAL INTERSECTION IN NO_2: INTERPRETATION OF ICLAS, LIF AND LIDFS SPECTRA WITH A MODEL HAMILTONIAN

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Using ICLAS, combined with a supersonic slit jet, we have observed and analyzed numerous vibronic cold bands of the $A^2B_2 \leftarrow X^2A_1$ transition in NO_2 in the near IR. The vibronic energies, relative intensities and rotational constants have been measured. Previous LIDFS results gave most X^2A_1 levels and few A^2B_2 ones up to about 11700 cm^{-1}. Due to the $X^2A_1 - A^2B_2$ conical intersection, the A^2B_2 and X^2A_1 vibronic levels are vibronically mixed. The zero order X^2A_1 and A^2B_2 levels interact according to their overall vibronic symmetry: A_1 (even n_3 for X^2A_1 states and odd n_3 for A^2B_2 states) or B_2 (odd n_3 for X^2A_1 states and even n_3 for A^2B_2 states). Due to the A^2B_2 vibrational frequency ratios ($\omega_1 \approx 2\omega_2 \approx 2\omega_3$) the A^2B_2 levels are clumped in polyads labeled with the polyad number $P = 2n_1 + n_2 + n_3$. Only the levels of B_2 vibronic symmetry are accessible by ICLAS, while both A_1 and B_2 symmetries can be detected by LIDFS. The complete set of 305 levels has been observed and assigned up to the $P = 2$ polyad (11700 cm^{-1}). The three A^2B_2 levels of the $P = 2$ polyad -(1, 0, 0), (0, 2, 0) and (0, 0, 2)- have been identified at 10999, 11210, 11283 cm^{-1} respectively. These values lead to $\omega_1 \approx 1265$ cm^{-1} and $\omega_2 \approx 738$ cm^{-1} for the symmetric stretch and bending frequencies respectively. In addition, four other levels with a dominant X^2A_1 character have also been observed in the same energy range by ICLAS and assigned to the X^2A_1 or A^2B_2 electronic states on the basis of their rotational constants, which are very different for the two zero order states. One unexpected result is the low value of the frequency of the A^2B_2 antisymmetric stretch ($\omega_3 \approx$ 775 cm^{-1}). The vibrational assignments were performed by the help of an effective Hamitonian, whose parameters have been fitted against the full set of 298 X^2A_1 levels and seven A^2B_2 located up to 11700 cm^{-1}. This Hamiltonian is formed by two diagonal parts, describing respectively the three vibrational modes of the X^2A_1 and A^2B_2 states, plus an off diagonal vibronic coupling, λq_3, where q_3 is the antisymmetric normal mode coordinate. As a result, in addition to the 22 vibrational parameters for the X^2A_1 state and the seven vibrational parameters for the A^2B_2 state, a new value of $\lambda = 340$ cm^{-1} was obtained. This model hamiltonian can be extrapolated to higher energies, where numerous vibronic levels have been observed and where vibronic chaos is well developed.

MULTI-DIMENSIONAL ANHARMONIC RESONANCES AND PARITY VIOLATION IN CDBrClF

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Parity violation causes rovibrational frequency shifts in infrared and microwave spectra between the corresponding lines of enantiomers of chiral molecules [1]. In previous theoretical treatments of this effect simple harmonic and anharmonic adiabatic approximations were used which assumed that the vibrational potential as well as the parity violating potential are separable in normal (or local) coordinates [2]. In the present work [3] we investigate in detail the influence of nonseparable anharmonic couplings on vibrational frequency shifts caused by the parity violating potential in CDBrClF. We use the strongly coupled four dimensional CD- and CF-chromophore subspace [4] and discuss how relative frequency shifts are influenced by coupling in the pure vibrational potential as well as in the parity violating potential. A four dimensional parity violating potential energy hypersurface has been determined ab initio and fitted to a polynomial expansion. We analyze the nonseparable multi-dimensional representation of the parity violating potential in a chiral molecule. The effects of the multi-dimensional anharmonic couplings provide the dominant corrections. These corrections can be more than a factor of two for vibrational frequency shifts, depending on the mode considered. This is of importance for future theoretical analysis of possible, although until now unsuccessful attempts to measure such frequency shifts by high resolution spectroscopy [5–7] (in the microwave and IR spectra).

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TEST OF ABSORPTION LINE SHAPE MODELS: AN ILLUSTRATION FROM MILLIMETER, SUB-MILLIMETER AND INFRARED SPECTRA OF HCN

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For the purpose of monitoring minor atmospheric species, reliable properties of line profiles are required. Now, it is well established that isolated absorption lines can exhibit significant deviations from the usual Voigt profile (narrowing and/or asymmetry) that are assigned to the correlation between molecular motions and collisions. The two main processes involved (velocity and/or speed changing collisions, speed dependence of relaxation rates) can be described separately by the Galatry profile or by the speed dependent Voigt profile, respectively, or jointly by the speed dependent Galatry profile. In most cases, all these models perfectly fit observed lineshapes, so that it seems impossible to retrieve the relative importance of narrowing processes from experimental records only.

In order to analyze this problem, we compare experimental results obtained on the HCN spectrum in various spectral ranges (the ν_2 band around 715 cm^{-1} [a] and the 354 GHz rotational line) or using a time domain technique (coherent transients on the 86 GHz $HC^{15}N$ line).

It is observed that, depending on the line shape model considered, narrowing parameters can exhibit unexpected behavior versus the sample pressure. Namely, non-linear pressure dependences of the diffusion parameter involved in the Galatry profile have been demonstrated, including possible failures of this profile in the collisional regime. By contrast, perfect linear behaviors of the narrowing parameter involved in the speed dependent Voigt profile are demonstrated for whole pressure ranges studied.

These results give an experimental evidence that observed departures from the Voigt profile are mainly related to the dependence of relaxation rates on molecular speeds and that molecular diffusion plays a minor role. These experimental findings are well explained by consideration of the polarization correlation function. They are well understood from the comparison of collisional

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optical and Lennard-Jones kinetic radii, and confirmed from Anderson-type collisional calculations.

As a conclusion, this study gives new insights on previous observations made in the infrared (namely on CO) and millimeter ranges, and allow to suggest that the speed dependent Voigt profile should be prefered to the Galatry profile for atmospheric applications.

LINE MIXING EFFECTS IN THE CF_4 VIBRATION-ROTATION SPECTRA

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Line mixing effects were studied thoroughly for linear molecules. We chose CF_4 in order to explore spectra of a tetrahedral molecule with higher weight than that of methane. The latter was an object of numerous studies and it was interesting to find out the difference between these two species.

Due to the dense tetrahedral structure and high molecular weight of the CF_4 molecule, it was impossible to resolve individual vibration-rotation lines. However, effective broadening coefficients for J-manifolds can be determined with reasonable accuracy for the ν_4 band. These values were found for He, Ar, and N_2 as perturbing gases. Obtained broadening coefficients decrease with manifold number m as one usually observes and the broadening coefficient behavior is similar to that previously registered for linear molecules.

Q-branch broadening is different from those for J-manifolds because of line mixing effect. First of all, the values of branch broadening are an order of magnitude smaller. Collisions with argon and nitrogen broad Q-branch in the ν_4 and ν_2 band almost 3 times more effective than collisions with helium. Also it is interesting to note that broadening by nitrogen is very close to result for argon though they are different for J-manifolds.

The found parameters were used in the band shape calculation for the higher gas pressures. To consider line mixing effect we used the following expression for band shape

$$K(\omega) = \frac{4\pi\omega}{3\hbar c}\left(1 - e^{-\frac{\hbar\omega}{kT}}\right) \cdot \mathbf{Re} \sum \rho_k d_k d_l \left[\frac{1}{i(\omega - \mathbf{L}_0) + \mathbf{W}}\right]_{kl}$$

where d_k and d_l are the reduced matrix elements for lines k and l; ρ_k is the population of the initial level of line k; $\mathbf{L}_0$ gives the diagonal line frequency matrix, and $\mathbf{W}$ is the relaxation matrix. The construction of this matrix is the main problem in the spectral shape calculation.

In this work we pay attention to the calculation methods developed for this matrix. The most fruitful investigations of this matrix were carried out with the CO_2 molecule as an example, and ECS model (sudden approximation with energy and adiabatic correction) was formulated for relaxation matrix calculations. However, it is very difficult to realise this approach for more complicated molecules such as CF_4. In the same time various empirical

models of relaxation matrix were developed. Thus, to calculate the band shape we constructed the **W** matrix as a linear combination of the strong collision rotational relaxation matrix and the relaxation matrix for weak interactions, which implies that only neighbouring lines interact. Such a matrix has given good results in band shape description.

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STRUCTURE AND BAND SHAPE EVOLUTION OF THE ν_2 FORBIDDEN BAND OF CF_4

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The infrared absorption spectra of CF_4 in mixtures with He, Ar and Xe were studied in the region of the ν_2 band, which gains its intensity from neighboring ν_4 fundamental band due to Coriolis interaction.

Several spectra of pure gas at pressures varied from 0.2 to 1.3 atm were obtained using a Bruker HR-120 instrument at the resolution of 0.02 cm^{-1}. This data allowed us to get necessary information about band structure and to check the consistence of literary data [1]. We determined the integrated intensity, which was found to be equal to 0.027(1) $cm^{-2}atm^{-1}$ at 293 K. Also a weak combination band situated at 415.7 cm^{-1} was observed.

The higher gas pressure part of this work has been performed using a Bruker IFS-28 spectrometer at 0.6 cm^{-1} spectral resolution. Pressure mixtures with Ar and He were varied from 30 to 100 atm and it was kept in the range of 30-72 atm for the Xe case.

The ν_2 band proved to be very sensitive to the type of intermolecular interactions at pressure increase. Spectra of mixtures with helium remain almost unchanged with pressure rise, only Q-branch gets slightly broader. We have detected no pressure dependence of integrated intensity in this case. However if we use argon as a perturber the integrated intensity increases. This effect becomes more pronounced in a pure gas or in the xenon mixture and the band profile changes tremendously. A broad unstructured component shifted from the band origin to higher frequencies appears with pressure increase. This is definitively a sign of induced character of the new component. We supposed this component to be a collision induced band, which appears due to quadrupole mechanism. The similar band was recently observed in CH_4-Ar spectra [2].

Further work will comprise an accurate retrieval of the rovibrational transition parameters and modeling of the band profiles.

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INTERCOMPARISON BETWEEN OZONE BROADENING PARAMETERS RETRIEVED FROM MILLIMETRE-WAVE MEASUREMENTS BY USING DIFFERENT TECHNIQUE

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It is well known that the pressure-broadening parameters are affected by systematic errors and it is difficult to determine what they depend on, and thus to recover them.

In the framework of a contract provided by the European Space Agency, linewidth measurements have been performed on selected rotational lines of ozone located between 300 and 320 GHz, in the B and C bands of MASTER platform. Broadening parameters have been determined for O_3 in collision with N_2 and O_2 at five different temperatures in the 190-300K range.

Experiments have been performed at LMSB and PhLAM by using both different experimental set-ups and different analysis procedures. At PhLAM, the video-type spectrometer used allows to observe the true lineshapes and compare them to Voigt and Galatry theoretical models. At LMSB, Galatry model has been used to analyse the second derivative of the natural line profiles recorded by using a frequency modulated spectrometer.

The two ozone lines, located near 302 and 317 GHz, observed in both laboratories allow us to make intercomparisons between the N_2- and O_2-pressure broadening parameters and their temperature dependence coefficients. In the whole, the results obtained in the two laboratories are in good agreement. Confidence intervals on these parameters will be also discussed.

HYPERFINE STRUCTURE OF S_2Cl_2

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Recently, chiral molecules are drawn much attention because an effect of the parity violation in molecules might be observable through an ultra high resolution spectroscopy [a]. The S_2Cl_2 molecule is one of such a molecule, which has YXXY-type structure with C_2 symmetry. IR spectroscopy of this molecule has been performed and all the vibrational bands have been studied experimentally and theoretically [b]. Marsden *et al.* have studied the rotational structure of the ground state with a Stark-modulation microwave spectrometer and have determined some molecular constants including the diagonal terms of the nuclear quadrupole coupling constants [c].

In this work, the rotational spectrum of S_2Cl_2 was remeasured by using Fourier-transform microwave spectrometer, which has much higher resolution than the previous work, because the evidence of parity violation would appear as very small shift in energy levels. In this measurement, the lowest rotational state ($J = 0$) was found to be splitting, which is normally degenerate by the first-order hyperfine interaction. We reanalyzed the spectrum with an effective rotational Hamiltonian concerning nuclear spin - rotation interaction and nuclear quadrupole interaction. In order to explain the unusual splitting, it is necessary to include all off-diagonal terms of the nuclear quadrupole interaction and to expand the rotational basis set up to $\Delta J \leq \pm 2$. Molecular spectroscopic parameters of rotational constants, centrifugal distortion constants, and nuclear quadrupole coupling constants including all off-diagonal terms for each Cl atom, thus determined, can reproduce 10 rotational transitions containing 141 hyperfine transitions with 4 kHz standard deviation.

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THE POTENTIAL ENERGY FUNCTION FOR THE ELECTRONIC GROUND STATE OF H_2Se DERIVED WITH THE MORBID APPROACH

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The potential energy surface for the electronic ground state of the hydrogen selenide molecule has been determined previously by P. Jensen and I. N. Kozin [*J.Mol.Spectrosc.* **160**, 39-57 (1993)] in a fitting to experimental data by means of the MORBID computer program. We report here a further refinement of this surface, also made with the MORBID program. There were two reasons for carrying out this work: 1) the number of vibrational states characterized experimentally for various isotopomers of H_2Se has approximately doubled since 1993, and 2) due to advances in computer technology fittings can now be carried out for energy levels with $J \leq 8$ whereas Jensen and Kozin could only use $J \leq 5$. In the present work, we fitted rotation-vibration energy spacings associated with

- 24 vibrational states of $H_2{}^{80}Se$ with $v_1 \leq 6$, $v_2 \leq 3$, and $v_3 \leq 6$,
- 11 vibrational states of $D_2{}^{80}Se$ with $v_1 \leq 2$, $v_2 \leq 3$, and $v_3 \leq 2$, and
- 17 vibrational states of $HD^{80}Se$ with $v_1 \leq 3$, $v_2 \leq 3$, and $v_3 \leq 3$.

The input data set comprised 3611 energy spacings.

In the fitting, we could usefully vary 29 potential energy parameters. The standard deviation of the fitting was 0.12 cm^{-1} and the root-mean-square deviation for 50 vibrational term values was 0.59 cm^{-1}.

Predictions made with the new potential surface have been used as starting point for the assignment of the super-weak bands $\nu_1 + \nu_2 + \nu_3$ and $2\nu_1 + \nu_3$ of the $HD^{80}Se$ molecule. For upper states with $J \leq 6$ the relative line positions are predicted with high accuracy (0.003-0.070 cm^{-1}). The theoretical values for the absolute transition wavenumbers are, however, all offset by a larger error (with order of magnitude 1 cm^{-1}) in calculating the band center. Consequently, we added to the theoretical values an offset which we varied in steps of 0.005, 0.010, and/or 0.020 cm^{-1}. For each value of the offset we obtained the number of experimental lines whose wavenumbers coincide with the calculated ones to within 0.005, 0.010, and/or 0.020 cm^{-1}, respectively.

By maximizing this number, we believe to have found the assignment of the rovibrational band.

As the final step of analysis, the assigned experimental lines were fitted with the effective Hamiltonian model both for lower and upper isolated vibrational states.

ALGEBRAIC HAMILTONIAN ADAPTED TO STRECH - BEND COUPLING IN THE STIBINE MOLECULE

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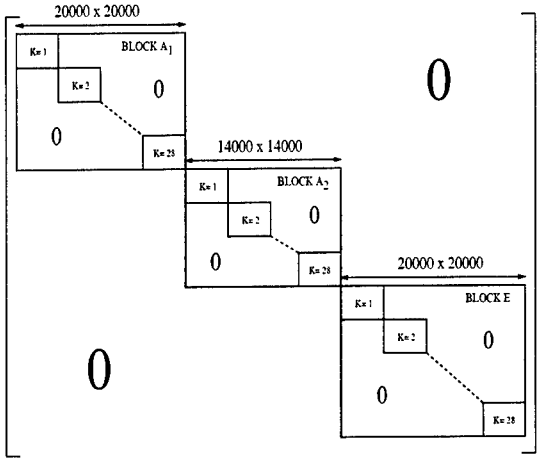
We explicite the unitary formalism $U(p+1)$ in molecular physics to study the strongly excited vibrational stretching and bending states of semi - rigid pyramidal molecules. The mathematical and physical properties are obtained through the group chain[1]:

$$(U_s(4) \supset U_s(3) \supset K_s(3) \supset S(3) \approx C_{3v}) \otimes (U_b(4) \supset U_b(3) \supset K_b(3) \supset S(3) \approx C_{3v}) \supset C_{3v}.$$

We determine a vibrational Hamiltonian describing the coupling beetween the stretching and bending modes of the XY_3 molecules. The coupling is characterized by the operator

$$H_{S-B} = \sum_{i=1}^{3} \sum_{j=5}^{7} \left(b_i^+ \, b_4 + b_j^{+\,2} \, b_8^2 + b_i \, b_4^+ + b_j^2 \, b_8^{+\,2} \right).$$

This operator induces the quantum number $K = 2n_s + n_b$ which labels the vibrational kets of the molecule. One deduces the following total algebraic Hamiltonian matrix :



We apply this formalism to the stibine molecule from 0 to 12000 cm^{-1}. The 23 known levels are reproduced with a standard deviation of 1.75 cm^{-1}. Moreover, the dissociation energy limit estimated with our formalism is close to the experimental one within 1%.

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VIBRATIONAL ENERGY LEVELS OF AMMONIA-TYPE MOLECULES WITH LARGE AMPLITUDE INVERSION MOTION

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We calculate variationally vibrational spectra of symmetric and asymmetric isotopomers of ammonia NH_3, hydronium ion H_3O^+, and phosphine PH_3. We use a new definition for the inversion coordinate and standard symmetry valence coordinates for the other degrees of freedom. The vibrational kinetic energy operator, which is exact within the Born–Oppenheimer approximation, is obtained using geometric algebra. The six-dimensional variational problem is solved effectively using successive basis set contractions and full symmetry of the systems. The six–dimensional potential energy surfaces, expressed as Taylor–like series expansions, are calculated with the CCSD(T) *ab initio* method and different correlation consistent basis sets up to the aug-cc-pV5Z quality. We employ basis set extrapolation and include core-valence correlation and first order relativistic effects to obtain estimates on different levels of theory for equilibrium geometries, inversion barriers and vibrational energy levels. The results agree well with experimentally observed values.

STEREOMUTATION DYNAMICS AND PARITY VIOLATION IN C_2 AND C_1 SYMMETRIC XYYX'(XYZX') TYPE MOLECULES

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In recent years we have investigated theoretically and experimentally a series of non-planar chiral molecules of the general C_1 and C_2 symmetric chain structures XYYX' or XYZX', where X and X' are two possibly identical isotopes of the same element (H and D for example) and Y and Z are chalcogenes such as O and S [1-6]. Examples are H_2O_2, H_2S_2 and in both cases their hydrogen isotopomers, as well as Cl_2S_2.

In this paper we extend this series with theoretical results for HSOH and its hydrogen isotopomers [7] as well as preliminary results for H_2Se_2 [8]. We present the mode selective full dimensional stereomutation wavepacket dynamics and parity violating energies. Parity violation in molecules has gained much interest recently because the predicted parity violating potentials are orders of magnitude larger [9,10] than previously calculated and therefore may be experimentally accessible in the near future.
The parity violating potentials were calculated using our multiconfiguration linear response approach in the random phase approximation [10]. The torsional tunneling stereomutation dynamics is investigated with the quasiadiabatic channel quasiharmonic reaction path Hamiltonian approach which treats the torsional motion anharmonically in detail and all the other coordinates as harmonic (but anharmonically coupled to the reaction coordinate) [4]. Our results will be discussed in relation to recent experiments [11] and compared with those of various other H_2O_2 type molecules. Furthermore, we discuss which of these molecules would be possible candidates for future measurements of parity violating energy differences.

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INTERNAL ROTATION OF THE NO_2 GROUP IN LOWER NITROALKANES: NITROETHANE

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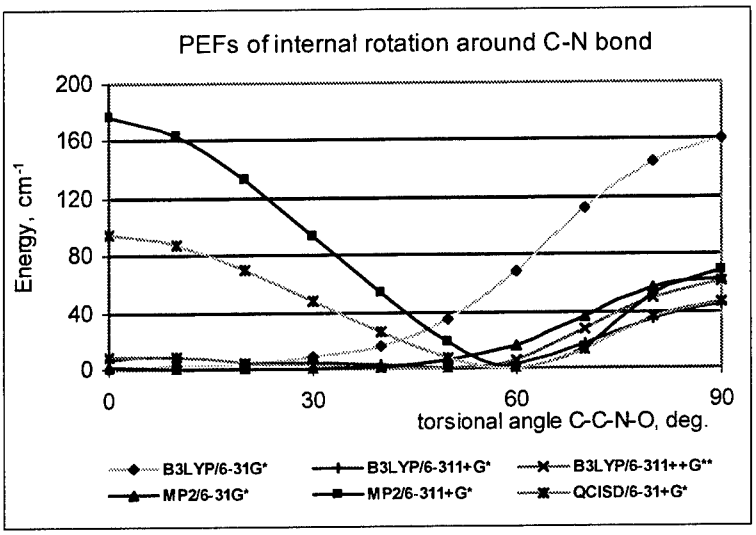
Potential energy functions (PEFs) of internal rotation around the C-C and C-N bonds in nitroethane have been investigated using the GAUSSIAN-98 program package. B3LYP, MP2, and QCISD quantum-chemical methods and 6-31G and 6-311G basis sets have been applied.

The internal rotation around the C-C bond is essentially frozen at τ(H-C-C-N)=60° (staggered position of methyl group), with barrier height varying in the range of 800-1200 cm^{-1}. The PEFs of internal rotation around the C-N bond are essentially different (see Fig.). All B3LYP calculations predict a broad and shallow minimum with the center at τ(C-C-N=O)=0° (the C-C bond is eclipsed with respect to the N=O bond), whereas MP2/6-311+G* and QCISD/6-31+G* calculations predict the minimum at about 60°. In all cases the barrier height is very low, resulting in approximately free internal rotation around the C-N axis.

Since the electron diffraction intensities are sensitive to the averaged mutual positions of atoms, we tried to determine the equilibrium geometrical parameters as well as to choose the shape of PEFs using the gas-phase experimental data. However, in this case the experimental intensities are consistent with each examined potential energy curve, corresponding to slightly different geometrical parameters. It seems that high-resolution molecular spectroscopy investigations are the only way to solve the problem of the internal rotation in nitroethane.


PEFs of internal rotation around C-N bond
Energy, cm-1
200
160
120
80
40
0
0
30
60
90
torsional angle C-C-N-O, deg.
B3LYP/6-31G*
B3LYP/6-311+G*
B3LYP/6-311++G**
MP2/6-31G*
MP2/6-311+G*
QCISD/6-31+G*

INTERNAL ROTATION ANALYSIS OF THE FT-MW SPECTRUM OF EIGHT ISOTOPOMERS OF DIMETHYL DISELENIDE

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The rotational spectra of eight isotopomers of dimethyl diselenide, CH_3Se $SeCH_3$, were recorded between 6 and 18 GHz with a pulsed-beam Fourier-transform microwave spectrometer. All rotational transitions of the symmetric isotopomers with C_2 symmetry, $CH_3{}^{78}Se{}^{78}SeCH_3$ and $CH_3{}^{80}Se{}^{80}SeCH_3$, are split into four components because of the interaction with the internal rotation of the methyl groups. The rotational transitions of the asymmetric isotopomers $CH_3{}^{76}Se{}^{80}SeCH_3$, $CH_3{}^{77}Se{}^{80}SeCH_3$, $CH_3{}^{78}Se{}^{80}SeCH_3$, $CH_3{}^{78}Se$ $^{82}SeCH_3$, and $CH_3{}^{80}Se{}^{82}SeCH_3$ are split into five components. The spectra for these isotopomers (100 to 125 frequencies each) were fit with experimental precision (1.5 kHz) to the effective rotational Hamiltonian for molecules with two periodic internal motions [a]. The fits required eight rotational and quartic centrifugal distortion constants and five or nine internal rotation and tunneling parameters for the symmetric or asymmetric isotopomers, respectively. For $CH_3{}^{80}Se{}^{80}SeCH_3$, the principal results were: A = 5156.15730(41) MHz, B = 1481.13557(56) MHz, C = 1420.13993(60) MHz, ρ = 0.013930(49), β = 36.554(52)°, α = 39.093(14)°, resulting in I_τ = 3.0816(80) u$\AA^2$. A similar fit was performed for $^{13}CH_3Se^{80}Se^{80}CH_3$ where fewer lines were measured due to the low intensity of the spectrum recorded in natural abundance. Substitution parameters were calculated in the $CH_3{}^{80}Se{}^{80}SeCH_3$ isotopic frame using the $CH_3{}^{78}Se{}^{80}SeCH_3$ and $^{13}CH_3{}^{80}Se{}^{80}SeCH_3$ moments of inertia to give r_s(Se-Se) = 2.306(3) $\AA$, r_s(Se-C) = 1.954(6) $\AA$, θ(CSeSe) = 99.8(2)° and ϕ(CSeSeC) = 85.2(1)°. For $CH_3{}^{80}Se{}^{80}SeCH_3$, a barrier to internal rotation of 395 cm^{-1} was obtained.

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METHYL INTERNAL ROTATION IN SUBSTITUTED TOLUENES

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The internal rotation of the methyl group in toluene, $H_3C\text{-}C_6H_5$, is hindered by a very low six-fold potential with V_6=0.05837(9) kJ mol^{-1} [1]. The situation remains almost unchanged, if a substituent is introduced in para position. Dramatic changes occur when substituents are introduced in meta and even more in ortho position. In the latter case the potential is dominated by large three-fold (V_3) contributions.

Quite a large number of substituted toluenes have been studied by microwave spectroscopy in our own lab (e.g. o- [2], m-, p-cresol: $H_3C\text{-}C_6H_4\text{-}OH$; p-thiocresol: $H_3C\text{-}C_6H_4\text{-}SH$; o-chlorotoluene [3]: $H_3C\text{-}C_6H_4\text{-}Cl$; p-toluidine: $H_3C\text{-}C_6H_4\text{-}NH_2$) and at other places. We will compare the torsional barriers of different molecules which have been obtained by spectroscopic means and also by ab initio calculations.

If the substituent also undergoes large amplitude motions (internal rotation of OH, SH, NH_2, inversion of NH_2) interesting coupling effects with the methyl internal rotation occur. So we found for syn-o-cresol a barrier V_3=7.912(46) kJ mol^{-1} and for anti-o-cresol V_3=4.4256(14) kJ mol^{-1}.

Another topic is the equilibrium position of the methyl group. In those cases where a high torsional barrier is present, one hydrogen of the methyl group lies within the ring plane which is also a mirror plane for the two other hydrogens located above and below the ring plane. Ab initio calculations indicate, that the situation is different in toluene and some substituted toluenes with a very low torsional barrier. In these cases none of the methyl hydrogens is found in the ring plane and these molecules become chiral. This has a considerable influence on the group theory and also on the microwave spectrum.

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MILLIMETER-WAVE SPECTRA OF THE $^{12}C^{16}O$ AND $^{13}C^{16}O$ DIMERS: ASSIGNMENT AND PRECISE LOCATION OF ENERGY LEVELS

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In recent years significant progress has been made in solving some of the fundamental riddles associated with the CO dimer. Following the infrared observations and first assignments of the IR spectrum made by McKellar [1,2], the millimeter-wave spectra of normal ^{12}C and fully substituted ^{13}C carbon monoxide dimers, $(^{12}C^{16}O)_2$ [3] and $(^{13}C^{16}O)_2$, were measured in the frequency range 60 - 180 GHz strongly supporting the infrared study. In a close collaboration of our two laboratories, at Cologne and at Ottawa, we have succeeded in measuring, assigning, and confirming many new states discovered by using the technique of combination differences. More than 50 rotational levels of the ^{12}CO- and the ^{13}CO-dimers with $J = 0$ to 8 in the ground state are now accurately known. The levels can be classified into "stacks" which have symmetry classifications of either A^+/B^- or A^-/B^+, and K-values of either 0 or 1. For the normal isotope, therefore the symmetry and the nuclear spin statistics cause alternate rotational levels to be missing. For $(^{13}C^{16}O)_2$, all levels are present with an intensity alternation of 1:3 between the A and B symmetries. The energetically lowest of the stacks fixes the tunneling splitting of $(^{13}C^{16}O)_2$ to be 3.769 cm^{-1}, slightly larger than the $(^{12}C^{16}O)_2$ value of 3.731 cm^{-1}. In both isotopes, the lower stacks fall into two groups, characterized by larger (4.4 $\AA$) or smaller (4.0 $\AA$) intermolecular separations. The energy splitting between the ground states of these two isomers is 0.877 cm^{-1} in $(^{12}C^{16}O)_2$ and 1.285 cm^{-1} in $(^{13}C^{16}O)_2$. Even though a considerable amount of precise experimental data is now available for the ^{12}CO and the ^{13}CO dimers, we still have a rather limited theoretical insight into its structure and tunneling dynamics. An overview of the present status of research will be given.

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MICROWAVE SPECTROSCOPY OF OPEN-SHELL VAN DER WAALS COMPLEXES

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The high resolution microwave spectroscopy of open-shell complexes provides a valuable source of information on the nature of intermolecular interactions. It not only provides the structure of the complex and information on the intermolecular forces but it can also provide detailed information on electron reorganisation on complex formation. In this presentation, we shall revisit the microwave spectroscopy on Ar-NO. This yields a complicated spectrum showing evidence of the effects of orbital and spin angular momenta on the fine structure as well as hyperfine structure due the nitrogen nucleus. Recently observed new spectroscopic transitions show that the previous semi-rigid analysis[1] was inadequate. An alternative approach to model the spectrum has been to perform a full dynamical calculation of the motions of the monomers on an assumed potential energy surface. This permits a better description of the molecular energy levels and enables corrections to the potential surface to be made following a least squares fit to the spectrum.

Similar spectroscopic improvements have been made to the spectrum of the analogous Ne-NO complex. Here the dynamical corrections to the spectrum are far more important. An assignment has been made to many of the observed transitions and a preliminary intermolecular potential energy surface has been derived.

In addition, preliminary spectroscopic results on the microwave spectroscopy of the potentially reactive complex OH-CO will be presented.

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MICROWAVE SPECTROSCOPY OF THE WEAKLY BOUND COMPLEXES OF CHIRAL MOLECULES

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The interactions between chiral molecules play a very important role in biological systems. We have chosen to study such interactions via the microwave spectroscopy of Van der Waals dimers containing such chiral species. One of the simplest chiral molecules containing biologically important functional groups is butan-2-ol. Detailed results from the spectroscopy of several of the binary complexes of butan-2-ol will be presented.

In addition many molecules like ethanol are potentially chiral. The gauche conformer is distinct from its mirror image. However quantum mechanical tunnelling rapidly interconverts the two mirror forms. On formation of suitable molecular complexes this tunnelling motion can be quenched and the resulting induced chiral dimers can be studied. The results for three conformers of the ethanol dimer together with initial results for the isopropanol dimer and the ethanol-water dimer will be presented.

In all cases there are many conformations of the complexes present. Throughout high quality *ab initio* calculations have been performed to help aid assignments.

A MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE STUDY OF 2-METHYLPYRIDINE AND ITS COMPLEX WITH AR: STRUCTURE, ^{14}N NUCLEAR QUADRUPOLE COUPLING AND METHYL INTERNAL ROTATION

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The rotational spectrum of 2-methylpyridine (α-picoline) in the two lowest states of methyl internal rotation (m=0,1) has been recorded in the range from 4 -15 GHz with employment of a molecular beam Fourier transform microwave (MBFTMW) spectrometer. The high resolution and sensitivity of the MBFTMW-technique allowed to resolve hyperfine structures due to ^{14}N nuclear quadrupole coupling (nq-hfs) with high accuracy and to detect the spectra of the ^{15}N- and all ^{13}C-isotopomers. These investigations considerably extend the results from an earlier study on the normal species.[a] Some of the lines showed small splittings of some 10 kHz which can not be attributed to nq-hfs or internal rotation effects. The analysis of all spectra yielded ^{14}N quadrupole coupling constants, the potential parameter V_3 for the barrier hindering the methyl internal rotation, and - in particular - r_0, r_s, $r_m^{(1)}$ and $r_m^{(2)}$ structural parameters for the molecule.
We have also started to investigate the rotational spectrum of the weakly bound dimer of normal 2-methylpyridine with Ar. First results on the nq-hfs, methyl internal rotation and structure of the complex will also be presented.

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VIBRATIONAL ANALYSIS OF MEDIUM STRENGTH HYDROGEN BONDED HETERODIMERS : FTIR SPECTRA AND BAND CONTOUR ANALYSIS OF THE STRETCHING MODE OF H(D)F COMPLEXED WITH ORGANIC BASES

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In the last twenty years, very detailed spectroscopic studies of simple hydrogen bonded systems like the HF dimer and small H_2O polymers have highlighted the fundamental aspects of this type of intermolecular interaction, giving rise to the determination of reliable intermolecular potential energy surfaces. The development of high resolution absorption IR laser spectroscopy coupled to jet-cooled molecular beams, has led to direct observation of the inter- and intramolecular vibrational degrees of freedom in weakly bonded dimers such as HX (X = F, Cl) with HX, HCN, OCO, N_2 and N_2O, providing in a first step rovibrational constants and intermolecular frequencies depending of the excitation energy. In a second step these data have been exploited in order to elucidate the intermolecular potential surfaces which has opened the way for state resolved unimolecular dynamic processes such as vibrational predissociation, tunnelling splittings, vibrationally induced isomerization and intramolecular vibrational energy flow. The spectroscopic study of more strongly hydrogen bonded complexes (D_e = 3-10 kcal/mol) involving larger molecules generally suffers from thermal congestion due to the large density of vibrational states. In order to reduce the heterogeneous broadenings of the hot and combination bands and to distinguish them from the homogeneous broadenings involving single transitions (lifetime of the excited state), we have coupled a low pressure continuous supersonic jet or a cooled cell to a Bruker IFS 120 HR interferometer. The objective is to understand the coupled dynamics of the hydrogen bond by analysis of the ν_s stretching vibration of the HF/DF subunit complexed with a series of open chain or cyclic ethers and their thio homologues. The progressive reduction of the flexibility of the acceptor molecule has led to a reinterpretation of the broad band contours observed for the complexes such as $(CH_3)_2O$-H(D)X. In the case of the rigid complex $(CH_2)_2S$-H(D)F, the analysis of the cell and jet spectra in the temperature range 50-250 K reveals, with the support of band fitting simulations which reproduce the multiple hot band progressions in the ν_s region, that three intermolecular modes $\nu_{\delta i}$, $\nu_{\delta o}$ (in-plane and out-of-plane bending) and ν_σ (stretching) are strongly coupled to the H(D)F stretch with significant

negative anharmonic coupling constants. Rotational, vibrational and dynamical data derived from our analysis of low and medium temperature spectra are compared in order to point out some general tendencies of the structural and dynamic properties as well as the anharmonic coupling patterns within these hydrogen bonded heterodimers.

THE MICROWAVE SPECTRA OF THE COMPLEXES OF FLUORINATED BENZENES WITH WATER

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As water is the most important solvent occurring in nature, its dimers with organic compounds are of special interest and the analysis of the interaction between water and organic compounds is a first step towards an understanding of solvation processes. Information about the structure and internal dynamics of such complexes is contained in their rotational spectra. Using the techniques of molecular beam FT microwave spectroscopy, we recently studied the complexes of different fluorinated benzenes ($C_6H_{6-n}F_n, n = 1, 2, 3, 4, 6$) with water. Of special interest is the nature of the interaction between the two complex partners. In the case of hexafluorobenzene$\cdots$water the water molcule is located above the aromatic ring whereas the structures of the complexes with $n < 6$ are essentially planar. This difference in structure has a dramatic effect on the rotational spectra. The planar species show the spectra of asymmetric tops which are split in two tunneling states. However, the spectra of hexaflurobenzene follow roughly the pattern of a symmteric top but with an extensive fine structure. This fine structure results from the nearly free internal rotation of the water molecule within the dimer. The spectra and their analyses will be presented.

ROTATIONAL SPECTRA OF He_N-N_2O (N=3-12) QUANTUM CLUSTERS

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Pure rotational spectra of He_N-N_2O quantum clusters with N=3-12 were recorded with a pulsed molecular beam Fourier transform microwave spectrometer. The 'vertical', J-quantum number, assignments of the individual clusters was confirmed by microwave - microwave double resonance experiments. N number assignments were verified by careful consideration of the sample pressure and nozzle temperature dependencies of the line intensities. The obtained spectroscopic constants of the He_N-N_2O clusters are interpreted in terms of cluster structure and dynamics. We will present the observed trends of the spectroscopic constants and discuss the implications for the new concept of molecular superfluidity.

MILLIMETER-WAVE SPECTROSCOPY AND COUPLED CLUSTER CALCULATIONS FOR A NEW PHOSPHORUS-CARBON CHAIN: HC_5P

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The linear HC_5P molecule has been detected for the first time in the pyrolysis products of phosphorus trichloride and toluene mixtures. Its rotational spectrum has been investigated in the millimeter-wave region, from 78 to 195 GHz, for the ground state and for the low-lying $v_{11} = 1$ excited state of both normal and deuterated species, spanning J values from 44 to 114.[a] Subsequent pyrolysis experiments have shown that the yield of HC_5P can be improved by a factor of ten if toluene is replaced by cyclopentene. This allowed us to extend the study of the rotational spectrum of the normal isotopomer to 11 further vibrationally excited states which approximately lie between 150 and 650 cm^{-1}, namely $(v_6v_7v_8v_9v_{10}v_{11}) = (000002)$, (000003), (000010), (000020), (000100), (001000), (010000), (100000), (000011), (000101), and (001001). The anharmonic resonances which couple the (100000) stretching state with the (000020) and (000101) bending states, and the l-type resonances which occur between the different sublevels of a given bending state have been taken into account in the analysis of the spectra, which yielded determinations of the α_6, α_7, α_8, α_9, α_{10}, and α_{11} vibration-rotation coupling constants, and of the $x_{L(11,11)}$, $x_{L(10,10)}$, $x_{L(10,11)}$, $x_{L(9,11)}$, and $x_{L(8,11)}$ anharmonicity constants. The experimental work was assisted by coupled-cluster single double triple [CCSD(T)] calculations, performed using the cc-pVQZ basis, which provided accurate predictions for equilibrium structure, dipole moment, and a large variety of spectroscopic constants like harmonic vibrational wavenumbers, vibration-rotation coupling constants and l-type doubling constants. Excellent agreement between experiment and theory was observed.

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DIODE LASER SPECTROSCOPY OF CO_2 IN THE 1.6 μm AND 2.0 μm REGIONS FOR ATMOSPHERIC APPLICATIONS

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The Groupe de Spectrométrie Moléculaire et Atmosphérique of Reims in collaboration with the Service d'Aéronomie (Meudon) and the CEM2 (Montpellier) have developed near-infrared diode laser spectrometers to study CO_2 line intensities and broadening coefficients.

The 1.6 μm region is studied using a commercial telecommunication-type diode laser. 13 lines of the $(30^01) \leftarrow (000)$ band of CO_2 have been studied. Preliminary measurements of stratospheric CO_2 achieved in 2002 with the "SDLA" balloon spectrometer are presented.

The 2.0 μm region is studied using a new generation of lasers: antimonide-based quantum-wells diode laser from CEM2. One line of the $(20^01) \leftarrow (000)$ band of CO_2 has been studied at 2.052 μm. We demonstrate with this laser the possibility to detect CO_2 at ground level thanks to the JETDLAG laboratory spectrometer

SPECTROSCOPIC STUDY OF THE $(30^01) \leftarrow (000)$ BAND OF CO_2 WITH A DIODE LASER SPECTROMETER

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A diode laser spectrometer was used in the laboratory to study CO_2 line intensities and pressure broadening coefficients near 1.6 μm. The spectral region ranging from 6230 to 6250 cm^{-1} which is suitable for the *in situ* sensing of carbon dioxide in the lower stratosphere was studied using a commercial telecommunication-type diode laser.

Thirteen lines of the $(30^01) \leftarrow (000)$ band of CO_2 have been studied. Our intensity measurements are compared to previous results achieved with a Fourier-Transform Spectrometer. Our experimental results are further compared with the HITRAN and the CDSD databases (Carbon Dioxide Spectroscopic Databank created using the effective operator approach). Furthermore the broadening coefficients by N_2 and O_2 for the strongest transitions are also reported and analyzed.

HIGH-RESOLUTION INFRARED SPECTROSCOPY OF $BrNO_2$ ISOTOPOMERS

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The ν_2 fundamental bands of different isotopomers of $BrNO_2$ (a mixture of $^{79}Br^{14}NO_2$ and $^{81}Br^{14}NO_2$, a second mixture of $^{79}Br^{15}NO_2$ and $^{81}Br^{15}NO_2$, and a third sample of isotopically pure $^{79}BrN^{18}O_2$) located around 13 μm were recorded using high-resolution Fourier-transform infrared spectroscopy. More than 10000 lines (with $J \leq 80$ and $K_a \leq 30$) of $^{79}Br^{14}NO_2$, $^{81}Br^{14}NO_2$, $^{79}Br^{15}NO_2$, and $^{81}Br^{15}NO_2$ were assigned and reproduced with a RMS deviation of better than 5×10^{-4} cm^{-1} using a nonlinear least-squares fitting routine (Watson-type A-reduced Hamiltonian in the I^r representation). Preliminary results of the analysis of the spectrum of $^{81}Br^{15}NO_2$ that was recorded very recently at University of Wuppertal will also be presented. The determination of the ground-state rotational constants will be used for calculations of the substitution structure of nitryl bromide.

HIGH RESOLUTION FTIR STUDY OF THE COUPLED ν_2/ν_5 BANDS AND THE EQUILIBRIUM ROTATIONAL CONSTANTS OF $D_3Si^{35}Cl$

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The aim of ongoing work on $D_3Si^{35}Cl$ is to determine vibrational and rovibrational energies and moreover vibrational corrections to the ground state rotational constants in order to obtain the equilibrium structure of the symmetric top molecule silyl chloride. After previously the 1^1, 3^1, 4^1 and 6^1 levels of $D_3Si^{35}Cl$ have been studied, and the ground state constants including A_0 and D_K^0 have been determined, we now report on an investigation of the bands ν_2 and ν_5 at 701.94 and 688.90 cm^{-1}, respectively, using monoisotopic $D_3Si^{35}Cl$ material by means of high resolution (0.0024 cm^{-1}) FTIR spectroscopy. About 9000 lines have been assigned and fitted with an rms deviation of ca. 0.3×10^{-3} cm^{-1}. Along with strong Coriolis coupling, $\zeta_{2,5}^y = \pm 0.636$, negative intensity perturbation, numerous $\Delta G = \pm 3$ (r, α^{BB}) and $\Delta G = \pm 6$ (t resonance) interactions occur. These are induced by the strong Coriolis interactions between the near-degenerate 2^1 and 5^1 states. They are quantitatively accounted for by the adopted model. Experimental equilibrium rotational constants of $D_3Si^{35}Cl$ will be presented.

FTIR MEASUREMENTS OF $^{12}C^{16}O_2$ LINE POSITIONS AND INTENSITIES OF HOT BANDS NEAR 2.7μm

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The experimental set-up has combines a high resolution Fourier Transform Interferometer (BOMEM DA8) with a high temperature cell (1m long and double pass). Experiments have been carried out in the spectral range 3700-3750 cm^{-1} by using pure samples of CO_2 at a pressure of 5mbar at about 300 K, 500K and 700K. The interferograms have been recorded without apodization (resolution of $4\,10^{-3}cm^{-1}$). Line position and intensity data have been fitted by a non-linear least squares method. For the lowest temperature, comparisons have been made with the recent results of Malathy Devi et al. [a]. The agreement is good. The highest temperature measurements have allowed us to characterize other hot bands. Significant differences with HITRAN2000 [b] have been found for the bands 14411← 04401, 21112←12202 and 22211←12201. These bands have been assigned using the calculations of Aguir at al. [c].

1. V. Malathy Devi et al., J. Quant. Spectrosc. Radiat. Transfert, **60**, 741(1998)
2. L.S. Rothman et al., to appear in J. Quant. Spectrosc. Radiat. Transfert.
3 M. B. E. Aguir et al.,J. Mol. Spectrosc. **215**,234 (2002).

NOBLE GAS - NOBLE METAL CHEMICAL BONDING? MICROWAVE SPECTRA AND GEOMETRIES OF KrCuF, KrCuCl, XeAgF AND XeAgCl

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The rotational spectra of several isotopomers of each of the complexes KrCuF, KrCuCl, XeAgF and XeAgCl have been measured using a cavity pulsed jet Fourier transform microwave spectrometer. The samples were prepared by laser ablation of Cu or Ag metal in the presence of Kr and SF_6, Kr and Cl_2, Xe and SF_6, and Xe and Cl_2, respectively, and were stabilized in supersonic jets of noble gas. The geometries of the complexes have been determined from the rotational constants. The spectral analyses have shown that (i) the complexes are much more rigid and strongly bound than normally found for van der Waals complexes; (ii) the noble gas - noble metal bonds are short compared to the sums of the noble gas van der Waals radii and the noble metal (I) ionic radii; (iii) there is significant charge rearrangement on complex formation, on both the noble gas and noble metal atoms (from ^{83}Kr, ^{131}Xe, ^{63}Cu and ^{65}Cu nuclear quadrupole coupling constants). The results, which are supported by *ab initio* calculations, give a strong indication of the presence of weak noble gas - noble metal chemical bonding.

Invited Lectures K

Thursday, September 11, 9:00

Chairman : M. HERMAN

EXPERIMENTS WITH QUANTUM DEGENERATE POTASSIUM-RUBIDIUM MIXTURES *(45 min.)*

M. INGUSCIO, *Dipartimento di Fisica and European Laboratory for Nonlinear Spectroscopy (LENS), Universitá di Firenze, Italy*

We investigate the properties of mixtures composed by potassium and rubidium atoms. Potassium isotopes are cooled down to quantum degeneracy by means of sympathetic cooling with rubidium [1]. Collisional interactions play a relevant role for both Bose-Bose (^{87}Rb-^{41}K) and Bose-Fermi (^{87}Rb-^{40}K) mixtures. For instance the strong attractive Bose-Fermi interaction has been shown to overwhelm the mutual repulsion between fermions [2]. New scenarios are opened by the control of the scattering resonances by means of external magnetic fields possibly allowing the formation of ultracold heteronuclear molecules [3]. This fascinating field of the formation and spectoscopy of ultracold molecules [4] will be discussed in the frame of recent results obtained in different laboratories.

[1] G. Modugno *et al.*, Science **294** (2001) 1320
[2] G. Modugno *et al.*, Science **297** (2002) 2240
[3] A. Simoni *et al.*, Phys.Rev.Lett. **90** (2003) 163202
[4] For a perspective see: M.Inguscio, Science **300** (2003) 1671

PLANAR PLASMA EXPANSIONS AS A TOOL FOR HIGH RESOLUTION SPECTROSCOPY *(20 min.)*

HAROLD LINNARTZ, *Fysische Chemie, Vrije Universiteit Amsterdam, De Boelelaan 1083, NL 1081 HV Amsterdam, the Netherlands*

Transient molecules, typically molecular radicals and ions, belong to the chemically most reactive species. This complicates systematic high resolution spectroscopic studies, as it is hard to generate large abundances under laboratory controlled conditions. In addition, plasma techniques are needed, that typically carry a large amount of excess energy, resulting in high vibrational and rotational temperatures. Under such conditions spectra of even simple systems can become rather complicated.

A solution for such problems is found by combining plasma and supersonic expansion techniques. Particularly two-dimensional expansions through a long and narrow slit are interesting: these offer a Doppler free environment and combine high molecular densities and large absorption pathlengths with an effective adiabatic cooling.

This presentation shows in detail how planar plasma expansions are generated and how the combination with sensitive spectroscopic techniques - such as cavity ring down, plasma-frequency double modulation or production modulation spectroscopy [1] - allows high resolution *direct absorption* spectroscopy of electronic, vibrational and pure rotational transitions of molecular radicals and ionic complexes.

The performance of different slit jet plasma sources is demonstrated on the example of rotationally resolved spectra of carbon chain radicals, such as the $A^2\Pi$-$X^2\Pi$ electronic transition of the linear C_6H radical and the dicyanodiacetylene cation NC_6N^+ [2] - and for rovibrational spectra of small cluster ions, such as the charge transfer complex $[Ar\text{-}N_2]^+$ [3].

[1] Rev. Sci. Instrum. 70 (1999) 1305; Rev. Sci. Instrum. 71 (2000) 1811; Chem. Phys. Let. 313 (1999) 171; Chem. Phys. 283 (2002) 119.
[2] J. Mol. Spectrosc. 197 (1999) 1; J. Chem. Phys. 116 (2002) 924.
[3] Science 297 (2002) 1166.

MILLIMETER WAVE SPECTROSCOPY OF HIGH RYDBERG STATES *(20 min.)*

ANDREAS OSTERWALDER, *Department of Chemistry, University of California, Berkeley, CA 94720, USA*

Modern methods in cation spectroscopy often rely on the excitation and detection of high Rydberg states (principal quantum number $n > 100$). A full characterization of such methods therefore requires a high level of understanding of the properties of these electronically excited states.

However, spectroscopic investigations of high Rydberg states are difficult because of the density of states (the energy level spacing between Rydberg states with n=100 and 101 amounts to ca. 0.2 cm^{-1}) and the sensitivity of these states to external perturbations (for example electric fields). In addition, most molecules require VUV radiation to excite and investigate these states. VUV-millimeter waves double resonance spectroscopy enables the investigation and characterization of high Rydberg states with principal quantum number $n \gg 100$ at a spectral resolution of 60 kHz (2 10^{-6} cm^{-1}).

This talk will include a description of the experimental method and a demonstration of its applicability to the spectroscopy of high Rydberg states and of molecular cations. By taking highly resolved spectra of ns, np, nd, and nf Rydberg states of ortho-H_2 in the range $n = 50 - 65$ and extrapolating the recorded Rydberg series using MQDT calculations, the hyperfine structure of the rovibronic ground state of the ortho-H_2^+ cation was determined with a precision of better than 1 MHz. In addition, the experimental data enabled the determination of precise values for the quantum defects of the observed series.

The speaker thanks the Swiss National Science Foundation for a postdoctoral fellowship.

Poster Session L

Thursday, September 11, 11:00

COLD COLLISIONS WITH RYDBERG ATOMS

ANDRÉ LUIZ DE OLIVEIRA, *Departamento de Física, Universidade do Estado de Santa Catarina, CP 631, 89223-100, Joinville, Santa Catarina, Brazil*; **M. W. MANCINI, V.S. BAGNATO and L. G. MARCASSA**, *Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, São Paulo, Brazil*

Recently cooling and trapping techniques were applied to experiments involving Rydberg atoms. In this work we measure the time evolution of the population resulting from energy transfer collisions as a function of the energy difference between the entrance and exit collisional channels using a sample of cold Rydberg atoms produced in a rubidium magneto-optical trap. The $34S_{1/2}$ population, produced by collisions between atoms in $33P$ state, is monitored as a function of time through the pulsed-field ionization technique. The experimental results are compared with a recent published model based on a two-body interaction considering an attractive potential [1]; which is calculated according a recent letter by C. Boisseau et al. [2]. The agreement is remarkable, which suggests the existence of such ultralong range potential proposed by C. Boisseau et al..

The details about our experimental setup and detection technique are described elsewhere [1]. Briefly, the cold Rb atoms are excited by a pulsed dye laser (1mJ/pulse, 4 ns, repetition rate 20 Hz,$\lambda \sim$ 480nm) pumped by the third harmonic of a Nd:YAG laser, from the $5P_{3/2}$ state. The Rydberg states are detected by pulsed field ionization. By varying the delay between the optical excitation and the high voltage pulse, we are allowed to observe the time evolution of the $34S_{1/2}$ state population. This collision process is studied as a function of the energy difference between the entrance and exit collisional channel, the energy difference is tuned by applying a static electric field using the Stark effect. The time evolution of the $34S_{1/2}$ state population is dominated by spontaneous decay and by the ultralong range potential. Our model suggests that atoms separated as much as $100.000a_0$ can contribute for this collisional process. By modeling our results we can extract the potential parameters and compared them with the ones calculated by C. Boisseau et al..The agreement is remarkable, suggesting the existence of such potentials and very large quasi-molecules. This work has received financial support from Fapesp and CNPq - Brazilian Agencies.

References

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[2] Christophe Boisseau, Ionel Simbotin, and Robin Côté, Phys. Rev. Lett.**88**, 133004 (2002)
[3] A.L. de Oliveira, M.W. Mancini, V.S. Bagnato, and L.G. Marcassa, Phys. Rev. Lett.**90**, 143002 (2003)

CONTINUOS PRODUCTION OF HETERONUCLEAR COLD MOLECULES

M. W. MANCINI, G. D. TELLES, A. R. L. CAIRES, V.S. BAGNATO and L. G. MARCASSA, *Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, São Paulo, Brazil*

In the last decade, many experiments have been devoted to the study of excited-ground state collisions using a sample of trapped cold atoms [1]. Several theoretical studies have been published, proposing new experiments involving two different species of atoms trapped together: two BEC species and heteronuclear cold photoassociation [2]. The natural extension of those investigations is the experimental study of the heteronuclear photoassociation by laser spectroscopy techniques. In this work we present the first observation of cold ground state heteronuclear KRb molecules.

According to Wang and Stwalley [2] the K-Rb sample is one of the most suitable for photoassciation due to its high relative heteronuclear Franck-Condon factor; nevertheless high atomic density are required. The heteronuclear molecules ae formed in the trap by photoassociation followed by spontaneous decay. To detect the ground state molecule we ionized with a pulsed dye laser and detect the ions using a CPM [3]. Briefly, in the experiment there are a trapping and probe phases. During the probe phase the heteronuclear pairs, which were photoassociated during the trapping phase are photoionized by a pulsed laser (1 mJ/pulse, 4 ns, $\lambda \sim 603$ nm). The ions are collected by a channeltron and analyzed by a boxcar integrator gate. By time-of-flight the atomic ions can be discriminated from the molecular ions. We observe K_2, Rb_2 and KRb ions in our laboratory. The molecules temperature was measured to be around $150\mu K$. By scanning the frequency of a photoassociation probe laser, we shall be able to obtain the bound states of the KRb molecule, and extract important information like the scattering length, etc. The production of heteronuclear cold molecules opens up new possibilities in the electrostatic traps of molecules. This work has received financial support from Fapesp and CNPq - Brazilian Agencies

References

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[2] H. Wang and W. Stwalley, J. Chem. Phys. **108**, 5767-71 (1998).

[3] A. Fioretti et al., Phys. Rev. Lett. **80**, 4402-5 (1998).

SPECTROSCOPY OF SINGLE CO MOLECULES IN ^{4}HE-DROPLETS

KLAUS VON HAEFTEN, CARSTEN KRAUSE, STEPHAN RUDOLPH, ANDREAS RÜDIGER, MARTINA HAVENITH, *Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum, D-44780 Bochum, Germany;*
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The infrared absorption of CO molecules solvated in superfluid ^{4}He droplets has been investigated. A beam of He droplets is produced in a supersonic expansion of ^{4}He gas at a pressure of 40 bars through a small nozzle (5μm) which was cooled to 19 K. Under these conditions the He droplets contain on average ~3500 He atoms. 20 mm downstream the droplets pick up CO molecules at a partial pressure of $3 \cdot 10^{-5}$mbar. The doped droplets are excited in the IR spectral range using a lead salt diode laser beam which is aligned antiparallel to the molecular beam. Finally, the droplets are detected by means of a mass spectrometer. The absorption of IR photons leeds to evaporation of several hundred He atoms and is detected as a depletion in the mass spectrometer signal.

The spectrum displays a single line at 2145.41 cm^{-1} which is assigned as the R(0), v=1 $\leftarrow$ 0 transition. Other lines of the monomer do not show up because of the relatively large ratio between the rotational constant B and the temperature of the He droplets (0.37 K). The shape of the line is rather symmetric having a width of $\sim 0.035\,cm^{-1}$ (fwhm). For many molecules solvated in He droplets it has been observed that the rotational constant is 3 times lower than in the gas phase. If we assume that this would be valid also for CO we can deduce a vibrational shift of 0.88 cm^{-1} to the blue. This is in line with a recent theoretical study which predicts - depending on the method - a blue-shift of less or equal than 1 cm^{-1}. [a] It is interesting to note that the width of 0.035 cm^{-1} is about 5 times larger than that of OCS in He droplets.

[a] F. Paesani and F. A. Gianturco, *J. Chem. Phys.* **116**, 10170 (2002).

HIGH-RESOLUTION SPECTROSCOPY OF METHANE IN PARAHYDROGEN CRYSTALS: CRYSTAL FIELD INTERACTION OF DEUTERATED SPECIES

T. MOMOSE, H. HOSHINA, H. KATSUKI, *Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*

Solid parahydrogen is a novel matrix for isolation spectroscopy of atoms and molecules.[abc] Rovibrational motion of molecules embedded in solid parahydrogen is well quantized on account of the weak interactions in the crystal. Most of the observed spectral linewidths are one or two orders of magnitude sharper than those observed in conventional rare gas matrices. Ro-vibrational transitions of molecules in solid hydrogen observed by high-resolution spectroscopy are subjected to quantitative analyses by the use of the crystal field theory we have developed previously.[d]

Here, we discuss rovibrational states of methane and its deuterated species in solid parahydrogen in detail. The crystal field interaction depends on the shape and symmetry of molecules embedded in the solid. Partially deuteration of methane causes additional crystal field interaction, since the symmetry of partially deuterated methane is lower than that of CH_4 and CD_4. We will discuss the effect of deuteration on the crystal field interaction obtained from the analysis of high-resolution spectra of ro-vibrational transitions of methane and its deuterated species.

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[d]T. Momose, J. Chem. Phys. **107**, 7695 (1997).

EPR SPECTRA AND ROTATION OF METHYL ISOTOPOMERS IN LOW TEMPERATURE MATRICES

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EPR spectra of CH_3, CHD_2, and CD_3 radicals have been observed in H_2, D_2 and Ne matrices in the temperature range 1.6 - 4.2 K. The radicals were obtained by condensation on a cold substrate of two gas flows: deuterium mixed with 4 mol% (in experiments with D_2 matrix), 2 mol% (in experiments with H_2 matrix), or about 30 mol% (in experiments with Ne matrix) methane passed through a discharge and pure H_2, D_2 or Ne avoiding the discharge. Though the result spectrum was a superposition of the spectra of the CH_3, CH_2D, CHD_2, and CD_3 radicals, we were able to study these simultaneously, i. e. under the same experimental conditions, which was due to the fact that the EPR lines were rather narrow: 0.86 G, 1.15 G, and 0.2 G in H_2, D_2 and Ne matrices, respectively. We have estimated the yields of the deuterated methyl radicals in reference to the CH_3 yield. These were found to be 35:1 for CD_3, 2:1 for CHD_2 and 1.3:1 for CH_2D. Thus, we conclude that methane in our discharge was almost completely deuterated through the intermediate products, CH_2D and CHD_2 to the final CD_4 one. At the substrate temperature of 4.2 K, the spectra of CD_3 in D_2, CHD_2 in Ne and both CD_3 and CHD_2 in H_2 were found to be a superposition of two spectra: high-temperature and low-temperature. A transformation of the shape of the CD_3 spectrum in all these matrices and CHD_2 spectrum in Ne and H_2 with decreasing sample temperature to about 1.5 K was observed. This is attributed to a change in the populations of the lowest rotational states of the radicals and, thus, testifies a reduction of the energy gap between J=0 an J=1 rotation levels of the trapped radicals. This data was compared to known results for deuterated methyl radicals in Ar [a] and suggested an existence of a hindering barrier for the radical rotation in solid H_2, D_2 and Ne.

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REACTIVITY OF THE NITRIC OXIDE + METHYL CHLORIDE SYSTEM ISOLATED IN ARGON MATRIX

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It is currently admitted that CH_3Cl does not react spontaneously with NO. The aim of this work is to check to which extent such an assertion can be considered as valid. For this purpose, mixtures of NO and CH_3Cl were isolated in solid argon matrices at low temperature and the reaction products were analyzed by vibrational FTIR spectroscopy. It was observed that one van der Waals complex is spontaneously produced. Furthermore, concentration effects demonstrated that this complex involves one CH_3Cl and two NO molecules which corresponds to $CH_3Cl\ (NO)_2$ stoechiometry. UV-visible photoexcitation of this complex yielded four new species. $^{14}N/^{15}N$ and $^{16}O/^{18}O$ isotopic effects on these species were analyzed. It appeared that C-H, C-Cl and N-O vibrational modes behave differently from one species to the other. Two of them exhibit reversible conversion by photo-selective UV-visible excitation. The detailed identification of these photoproducts is in progress.

A FREQUENCY ANALYSIS OF THE ν_9 BAND OF CD_3CD_3: EXPERIMENT AND AB INITIO CALCULATIONS

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The infrared gaseous spectrum of CD_3CD_3 has been measured in the range of 530-670 cm^{-1} to investigate vibration-torsion effects in the ν_9 band. Three separate spectra all taken under different experimental conditions were recorded. The lines with $\Delta K = -1$ and with high values of K show torsional splittings that are substantially larger than expected from the observed barrier height. These splittings are caused primarily by Coriolis-type interactions between the torsional stack of ν_9 and the corresponding stack for the ground vibrational state. Because of a near-degeneracy that exists between the states ($v_9 = 1, v_4 = 0$) and ($v_9 = 0, v_4 = 3$), three subbands $(K, \sigma) = (15, 1), (16, 2), (17, 3)$ are resonantly perturbed. For these cases, perturbation-allowed $3\nu_4$ torsional transitions have been identified. Here $\sigma = 1, 2$, or 3 labels the torsional sublevels. Measurements from the ν_9 and $3\nu_4$ bands, frequencies from the far-infrared torsional spectra in the ground vibrational state, and lower state combination differences from $\nu_9 + \nu_4 - \nu_4$ band were fitted to within experimental uncertainty using an effective Hamiltonian which considered three torsional stacks; one for the ground vibrational state and two for . In all, 22 parameters were determined using a total of 2001 lines. Two barrier dependent torsion-rotation parameters that were essential for obtaining a satisfactory fit were calculated by ab initio methods.

AB INITIO STUDY OF ELECTRONIC STATES OF METAL-BENZENE MOLECULES

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Ab-initio calculations have been performed to examine the low-lying molecular states of *3d* transition metal benzene complexes (MC_6H_6 with M=Sc, V and Ni). Despite recent experimental and theoretical efforts, the fondamental electronic state of these molecules is not fully characterized yet. The main difficulty to describe these systems is coming from the existence of open *d* electronic shells and of numerous low energy electronic states. In particular, the spin multiplicity of the ground state is difficult to determine and different theoretical approaches may lead to controversial results. In the present work, *ab-initio* complete active space self-consistent field plus multireference configuration interaction type calculations have been performed to investigate the potential energy profile of the electronic ground state and some lower-lying excited states. The lowest energy structures are found to be long range states while the short range states are found to be metastable with respect to the metal atom and benzene ground states. The theoretical results will be compared to recent dipole moment measurements by electric deflection experiments.

AB INITIO CALCULATIONS ON THE SF_5Cl MOLECULE

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The ν_8(e) stretching fundamental of the SF_5Cl molecule[a] is a perpendicular band, which is very dense and consequently quite difficult to analyze. For this reason, we have performed some ab initio calculations predicting the geometry of this molecule, its harmonic frequencies, dipole moment and rotational constants. All these molecular properties have been determined with the GAUSSIAN 98[b] program in four different basis which are MP2 6-31G(d,p), MP2 cc-PVDZ, B3LYP/6-311 G** and B3LYP/cc-pVTZ. We have then deduced the centrifugal distortion and first order coriolis constants thanks to the program INFRA of W. Thiel[c]. This set of data should lead us to a better interpretation of the ν_8(e) band.

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COMPLEXES WITH INORGANIC HYDRIDES (NH_3, PH_3, AsH_3)

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The optimal structures and harmonic vibrational frequencies of water complexes with NH_3, PH_3, AsH_3 have been determined by the Restricted Hartree-Fock (RHF) and second order Møller-Plesset perturbation theory (MP2) with augmented correlation consistent double zeta basis set for NH_3–H_2O, PH_3–H_2O complexes and 6-31++G(d, p) basis set for AsH_3–H_2O. At the MP2 level, this basis set yields very accurate results for the structure, dipole moment, and harmonic vibrational frequencies of water monomer. Analysis of the structural trends revealed that the separation between the neighboring oxygen atom and the X (N, P, As) atom increases in the row from N to As. The harmonic vibrational frequencies corresponding to OH_b ("bridge" hydrogen) stretches show large red shift by 224 cm^{-1} for the NH_3–H_2O complex, but for PH_3–H_2O and AsH_3–H_2O these shifts are about 20 cm^{-1}. The intensities corresponding to the OH_b stretches increase several orders of magnitude as a result of H-bonding. The intensity patterns are analyzed by means of electronic density redistribution, which reveals that intensification of the proton donor stretch is chiefly due to the increasing charge flux associated with H-bond formation.

AB INITIO STUDY OF THE $NH_3 \cdots H_2$ COMPLEX – FIRST SADDLE POINT OF INDEX TWO ON A REACTION PATH

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Ab initio CCSD(full)/6-311++G(3df,2p) calculations were performed for the bimolecular complex $NH_3 \cdots H_2$ and its rearrangements. The *ab initio* calculations performed predict the existence of sufficiently stable bimolecular complexes $NH_3 \cdots H_2$ with the very small complexation energy of about 0.02 kcal /mol. The tunneling splitting of the complex is much larger than that of NH_3. A peculiar topology of the potential energy surface is found around a saddle point of index two, and a valley-ridge-inflection point.

A SIMPLE APPROXIMATION TO VALLEY-RIDGE-INFLECTION POINTS ON POTENTIAL ENERGY SURFACES

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Valley-ridge-inflection points (VRI) of a potential energy surface (PES) may have a strong relation to the occurence of bifurcations along reaction pathways of a molecular rearrangement. We propose a procedure to calculate such points. For that, a mathematical connection between the following of a reduced gradient[a] and the calculation of gradient extremals (GE) for chemical reactions is derived. The tangent search method to follow a GE to the smallest eigenvalue[b] is extended to follow also other GEs in order to find a VRI point. The new method uses second derivatives of the PES only. qThe application to asymmetric VRI points of HCN is discussed.

Some programs are available online and free of charge through the web-side http://www.mathematik.uni-leipzig.de/MI/quapp

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IMPROVED VARIATIONAL CALCULATIONS OF THE VIBRATIONAL ENERGIES FOR NH_3 FROM HIGH-LEVEL *AB INITIO* POTENTIAL ENERGY SURFACES

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Recently[a] we have reported theoretical vibrational energies for the electronic ground state of the NH_3 molecule. Analytical potential energy surfaces were constructed from CCSD(T)/aug-cc-pVTZ *ab initio* data augmented by the results obtained by extrapolating CCSD(T)/aug-cc-pVXZ (X=T,Q,5) results to the complete basis set limit and adding corrections for core-valence correlation and relativistic effects. Vibrational energies were calculated with a variational model employing a kinetic energy operator expressed in terms of linearized internal coordinates. The exact internal coordinates were expressed as fourth-order Taylor expansions in the linearized coordinates. In the present work, we extend the Taylor expansions to sixth order and improve the *ab initio* surfaces by adding a large number of points on a regular grid and in low-energy regions beyond this grid. This leads to a significant improvement in the calculated vibrational energies.

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A NEW SEMI-EMPIRICAL POTENTIAL FOR AR-CO

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Due to the small dipole moment of the CO molecule induction plays a negligible role in the Ar-CO molecular complex. Ar-CO is therefore a suitable model system to validate the dispersion and exchange-overlap parts of the intermolecular potential derived from theoretical *ab initio* calculations. A comparison between the most recent *ab initio* studies[a] and the experimental work demonstrates a lack of sufficient agreement with strongest deviations[b] in the region around 25 cm^{-1}. Starting from the *ab initio* potential of Toczylowski and Cybulski[c], we have carried out a semi-empirical fit of the potential energy surface to all 7 known intermolecular modes. All modes could be reproduced within 0.2 cm^{-1} using our new potential energy surface. The most significant deviation which was found in comparison to previous *ab initio* potentials was the appearance of a second local minimum in the potential energy surface located at ($\Theta = 180°$), i.e. the collinear Ar-C-O configuration of the complex. These results indicate a lack of sufficient accurate theoretical description of intermolecular forces for Ar-CO which remains still a challenge for the future.

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THE ANALYSIS OF TEMPERATURE DISTRIBUTION IN AN END-PUMPED SOLID- STATE LASER FOR SPECTROSCOPIC APPLICATIONS

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End-pumped solid-state lasers have attracted a considerable attention for laser spectroscopy of atoms and molecules. In this respect, a very well qualified laser beam with known profile is usually needed for collection of precise spectroscopic data. Knowledge of distribution and change of refractive index of the laser rod is essential for monitoring the quality of the laser beam. In this work as first step, a theoretical investigation of temperature distribution and refractive index variations is performed. A partial differential equation governing temperature distribution T(r,z) is described as:

$$\frac{\partial^2 T(r,z)}{\partial r^2} + \frac{1}{r}\frac{\partial T(r,z)}{\partial r} + \frac{\partial^2 T(r,z)}{\partial r^2} = -\frac{S(r)}{k} \qquad (1)$$

where k is the thermal conductivity of the laser rod and S(r) is the pump source profile which is assumed to have a Gaussian shape:

$$S(r) = \frac{2P_{tot}(1-\eta\frac{\lambda_{pump}}{\lambda_{laser}})}{\pi w_0^2 L} e^{\frac{-2r^2}{w_0^2}} \qquad (2)$$

where P_{tot} shows the total power of the pump source, η is the quantum efficiency and ω_0 is the beam waist of the pump. One of the important aspect of this work compared to other researches is that no approximation has been made and the solutions were derived analytically. A complete and comprehensive solution of Eq(1) along the rod will be given.
The results were applied to various laser rods such as Nd:YAG, Nd:YVO_4 and Nd:YLF and will be compared to other works when they expose the laser rod to rather constant pump profile. The work is continued to quantify the effects of these temperature distribution on the beam quality of the laser.

A GENERAL METHOD TO GENERATE COLD RADICALS FOR STUDIES BY HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY: APPLICATION TO NH_2

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A general method of generating radicals in cold supersonic expansions in the gas phase is presented. The method relies on excimer laser photolysis of suitable precursor molecules in a thin quartz capillary mounted at the orifice of a pulsed gas nozzle and can easily be combined with vacuum ultraviolet photoionization mass spectrometry and high-resolution photoelectron spectroscopy. The characteristics of the radical source are described in detail and its performance is illustrated by mass spectrometric and high-resolution photoelectron spectroscopic investigations of NH_2, CH_2, CH_3, C_2H, C_2H_3 and C_2H_5.

As an application, rotationally resolved spectra of low vibrational levels of the $\tilde{a}$ state and of high bending vibrational levels of the $\tilde{X}$ state of NH_2^+ and ND_2^+ have been recorded for the first time by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy and the analysis of these spectra is presented.

NUCLEAR SPIN CONVERSION IN ELECTRIC FIELD: THE ROLE OF COLLISIONS

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When a gas sample of $^{13}CH_3F$ is prepared with a population of isomers (ortho and para forms) far from the equilibrium given by nuclear spin statistics, it relaxes towards this equilibrium with an exponential decay rate. This phenomenon called nuclear spin conversion is mainly governed by intramolecular spin-spin and spin-rotation interactions which can couple ortho and para states[a]. Two gateway pairs (J_o=9, K_o=3; J_p=11, K_p=1) and (J_o=20, K_o=3; J_p=21, K_p=1), for which energy difference lies below 1 GHz, have been identified and their role in the conversion experimentally confirmed[b]. In the presence of a static electric field, the degeneracy can be reached for Stark sub-levels with a corresponding increase of the nuclear conversion rate. Varying step by step the electric field, a conversion "spectrum" has been recorded experimentally (see Figure). The intensities of the peaks are directly related to the interaction strengths, their widths give an insight on the efficiency of the collisions to break the coherence between ortho and para levels created by the interactions. Such rates are directly extracted and will be compared to the rotationnally inelastic molecular collisions one.

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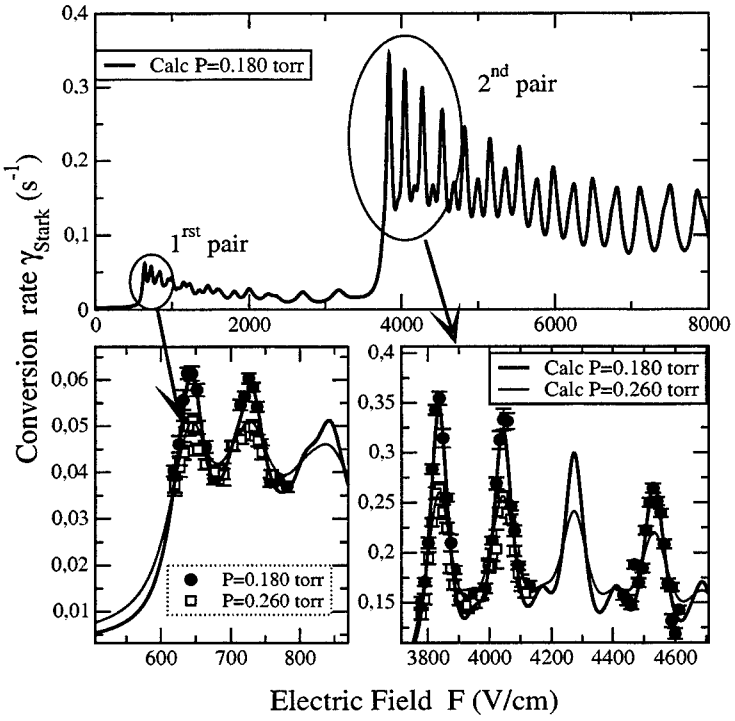
Calc P=0.180 torr
2nd pair
1rst pair
Conversion rate γStark (s-1)
P=0.180 torr
P=0.260 torr
Calc P=0.180 torr
Calc P=0.260 torr
Electric Field F (V/cm)

ROTATIONAL DEPENDENCE OF THE DIPOLE MOMENT OF CH_3F FROM THE MEASUREMENTS OF THE NUCLEAR SPIN CONVERSION SPECTRUM

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Methyl fluoride CH_3F is a molecule for which the rotational and vibrational dynamics have been extensively analysed thanks to gas phase high resolution spectroscopy. These studies allow to identify the gateways responsible for the modification of the total nuclear spin I of the equivalent H atoms in the molecule, i.e. the change $I = 3/2$ (ortho) and $I = 1/2$ (para). A gateway is a pair of ortho and para states coupled by a hyperfine, spin-spin or spin-rotation, interaction term in the molecular Hamiltonian. For a symmetric top molecule of C_{3v} symmetry and in the vibrational ground state, ortho states are identified by $K = 3n$ (n integer) and para states by $K = 3n \pm 1$. Due to the weak hyperfine coupling the gateway levels have to coincide closely, with an energy difference typically well below 1 GHz.

For $^{13}CH_3F$ two pairs ($J_o = 9$, $K_o = 3$; $J_p = 11$, $K_p = 1$) and ($J_o = 20$, $K_o = 3$; $J_p = 21$, $K_p = 1$) are mainly involved in the conversion process. Chapovsky[a] proposed a quantitative model which has been checked by several experiments. Among them, it has been shown that submitting CH_3F molecules to a Stark field leads to a change of the energy difference between the M-components of the interacting ortho and para levels and to an increase of the spin conversion rate[b].

In the present study we applied Stark fields up 15 kV/cm in order to cross the M-components of the second interacting level pair. For a quantitative reproduction of the conversion spectrum, i.e. the conversion rate in presence of a static electric field versus the strength of the field, it was necessary to take into account the rotational dependence of the dipole moment of CH_3F, which is expanded as $\mu = \mu_0 + \mu_J J(J+1) + \mu_K K^2$. The newly determined μ_J and μ_K parameters are compared to those expected using the Watson's centrifugal distortion dipole coefficients, which can be derived from the geometry, the

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force field, and the derivatives of the dipole moment with respect to either symmetry or normal coordinates of the molecule[c].

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INTERFACING THE ZURICH FTIR SPECTROMETER BRUKER IFS 120 HR (PROTOTYPE) WITH A COLLISONAL COOLING CELL

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We have interfaced a collisional cooling cell[a], containing a White-type cell with a maximum path length of 20 m, with our very high resolution Fourier transform infrared (FTIR) spectrometer, the Bruker IFS 120 HR (prototype, $\Delta\nu = 0.0007$ cm^{-1}). We were able to measure CF_3H in He for 10 h at 120 K in the 900-1300 cm^{-1} region with a resolution of $\Delta\nu < 0.001$ cm^{-1}. Spectra will be presented and will be compared to recorded spectra at room temperature and in supersonic jets[b].

In addition, we have used the setup to measure H_2O cluster spectra at 5 K with low resolution ($\Delta\nu = 1$ cm^{-1}). Oligomers of H_2O as well as smaller nanoparticles have been observed in the 3000-4000 cm^{-1} region.

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THE TIME RESOLVED IR-IR DOUBLE RESONANCE: A TOOL TO STUDY THE RELAXATION OF CH_4 MIXED WITH H_2, N_2, OR He AFTER EXCITATION INTO $2\nu_3$ AND TO DETECT NEW CH_4 HOT BAND LINES

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The experiments of Time Resolved IR-IR Double Resonance (TRIRDR), that consist in exciting the molecules of a gas into a selected rovibrational state and probing the time evolution of the population of this level and other ones after excitation, are precious tools both for relaxation studies and for finding new lines.

In our experiments the pump laser is an OPO producing pulses around 6000 $cm^{-1}$to excite CH_4 on a level of the $2\nu_3(F_2)$ state and the probe laser is a lead-salt diode laser emitting continuous radiation tunable in the 2940-2995 cm^{-1}range. By using this technique we have been able to observe the rovibrational relaxation of methane with various colliding partners: H_2, He, and N_2[a] at room temperature and 193K [b]. By probing $3\nu_3$-$2\nu_3(F_2)$ transitions in which the lower level is the laser-excited level, rotational depopulation rates were measured. The vibrational relaxation was investigated by probing other stretching transitions such as $2\nu_3$-ν_3, $(\nu_3+2\nu_4)$-$2\nu_4$, $(\nu_3+\nu_4)$-ν_4 transitions. A numerical kinetic model, taking into account many collisional processes connecting energy levels up to 6000 cm^{-1}, has been developed to describe the vibrational relaxation. The model has permitted to reproduce the observed signals corresponding to assigned probed transitions and to determine rate coefficients for various relaxation processes. The good agreement between computed and observed signals allows us to intend using this model to predict the time evolution of populations in case of pressure or mixing ratio conditions that cannot be realized in our experiments.

Also, the model can predict the temporal behavior of signals corresponding to many different transitions. Numerous signals have been observed at frequencies that are not currently assigned. Among them, various signals are doubtless corresponding to pentad-tetradecad transitions between A-symmetry levels. Indeed, these TRIRDR experiments make it possible to observe and to

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locate very precisely transitions that could not be observed by traditional spectroscopy and to propose their identification by comparing the temporal evolution observed for these DR signals with the temporal evolutions predicted by the kinetic model. Independent assignments of the located frequencies are necessary to further test the intermode processes introduced in the kinetic model.

SUBMILLIMETER-WAVE MEASUREMENTS OF THE PRESSURE BROADENING OF BrO, HO_2, AND O_3

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In the upcoming JEM/SMILES(a Superconducting Submillimeter-wave Limb Emission Sounder) and EOS-MLS missions key species which play crucial role in the chemistry of the upper atmosphere are planned to be continually monitored. For reliable retrieval of spatial distribution of key species from observational data, various types of spectroscopic parameters should be known with high accuracy. In this investigation, the pressure broadening parameters and their temperature dependences of BrO, HO_2, and O_3 have been critically examined.

The experiments were carried out independently at Ibaraki University and Jet Propulsion Laboratory. The line profiles of the $J = 23.5 \leftarrow 22.5$ and $J = 25.5 \leftarrow 24.5$ rotational transitions in the ground vibronic state $X\ ^2\Pi_{3/2}$ of ^{81}BrO at 624.768 GHz and 650.178 GHz were measured with O_2 and N_2 as foreign gases in the pressure range up to about 400 mTorr at Ibaraki and about 1.6 Torr at JPL. These BrO lines exhibit the hyperfine splittings of similar magnitude to the line width. Therefore we employed the convolution fitting routine devised by Pickett[a]. The results obtained at these two institutions agree very well, indicating that the data are not biased by systematic errors. The broadening coefficients for the HO_2 radical were determined reasonably well and again the values obtained at Ibaraki and JPL agree well. However, the temperature dependence has not been determined very well, in particular at temperature below -20 °C. The values presented here should be regarded preliminary.

Ozone lines including those from minor isotopes will dominate the atmospheric spectra. The line broadening parameters for 16 normal O_3 lines ranging from 195 GHz to 625 GHz were measured by the JPL group. One of the lines that is targeted by both SMILES and EOS-MLS at 625 GHz has been independently investigated at Ibaraki. The results from two groups again are in excellent agreements.

In the presentation, the details of the experimental procedures and the analysis will be discussed.

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ABSORPTION PROFILES OF HCl FOR THE $J = 1 - 0$ TRANSITION: FOREIGN GAS EFFECTS MEASURED FOR N_2, O_2, AND Ar

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The precise measurements on absorption line profiles are required for quantitative analysis of trace gases in the earth, planetary, and stellar atmosphere. Few data have been published so far in microwave and terahertz region because of technical difficulties. We have, therefore, concentrated our effort on developing high-precision measurement and analysis techniques in order to supply accurate profile parameters and pressure coefficients of molecules [1,2]. Hydrogen chloride (HCl), as well as $ClONO_2$, is a species of interest in atmospheric chemistry: a temporary reservoir of chlorine, which plays a principal role in the destruction of the stratospheric ozone layer. Although some line profile measurements have been carried out for the pure rotational transitions of HCl [3-5], parameters reported were not accurate enough for the environmental applications. In the present study, absorption profiles were measured precisely for the $J = 1 - 0$ rotational transition of $H^{35}Cl$ and $H^{37}Cl$, and the parameters for foreign gas effects were determined.

Absorption profiles have been recorded with the AIST Terahertz spectrometer [2,6]. The submillimeter-wave radiation was generated by a backward-wave oscillator. The radiation beam was mechanically chopped with a frequency of 230 Hz and the signal was detected by a lock-in amplifier in the $1f$ detection mode: the transmission spectra in real form were recorded. The sample gas was prepared in the absorption cell, a Pyrex glass tube with 131-cm length. Total gas pressure was measured by a Baratron gauge with 1 Torr full scale (1 Torr $\approx$ 133 Pa). The sample cell was first filled with HCl and then the foreign gas (N_2, O_2, and Ar) was added; total pressures were between 100−700 mTorr with concentration of HCl $\sim$ 2 %. The all measurements were carried out at room temperature.

By fitting the observed absorption profiles with the *modified* Voigt and the Galatry functions [7], the integral intensity parameter, the line center position, the Lorentzian width, and the Doppler width / the contraction parameter were determined. The foreign-gas effect was deduced from the line parameters obtained in the foreign-gas experiment by removing the self-effect. The partial pressure of HCl was evaluated from the observed integral intensity on the basis of the dipole moment [8].

The precision in the intensity measurements was better than 1 %. The

Lorentzian width shows a linear dependence on pressure. In the analysis with the *modified* Voigt function, the collisional narrowing effect is indicated by the fact that the Doppler width deceases significantly with increasing pressure. The pressure induced line shifts have been clearly observed.

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MODELING OF THE ROTATIONAL RELAXATION MATRIX IN LINE MIXING EFFECT CALCULATIONS

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The general formulation for overlapping line shapes prescribes to calculate the band shapes via the rotational relaxation matrix **W**, which elements depend on transition probability between rotational states of molecules under collisions. The most fruitful investigations of this matrix were carried out with the diatomic or linear molecules, and ECS model (energy corrected sudden approximation) was usually used for relaxation matrix calculations. Since it is difficult to expand the elaborated methods to top molecules containing thousands lines, various empirical models of relaxation matrix were developed. The simplest empirical method of relaxation matrix calculation uses the model of strong collisions. It is necessary only one collision (in average) to randomise the rotational states in this model. The model was modernised considering weakened branch coupling (ABC model [1]).

The ABC model provides good results for band shapes of pure gases or heavier gas mixture, but it is not the case of He or H_2 collisions. We explained this fact by the weakness of real collisions for these pairs. So, to calculate the band shape we constructed the **W** matrix as a linear combination of the strong rotational relaxation matrix and the relaxation matrix for weak interactions, which implies that only neighbouring lines interact. We computed the corresponding matrix elements from symmetry relations and sum rules.

This matrix was examined using the spectra of CO_2 molecule with different perturbing gases. It proved to be better to describe band shapes than the ABC model. Then the proposed model was applied to CF_4 spectra, which can not be interpreted using ECS model till now. Use of weak collisions in band shape calculations has provided good results for the spectra of CF_4-Ar and CF_4-He mixtures in the ν_4 band region. Analysing the matrix structure one can see that collisions are much weaker in the CF_4-He case.

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MODELING OF ABSORPTION IN CENTRAL AND WING REGIONS OF CO_2 IR BANDS. COMPARISONS WITH LABORATORY AND ATMOSPHERIC SPECTRA

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A theoretical model is proposed for the calculation of absorption by far line-wings in the region of ν_2 and ν_3 CO_2 bands. These spectral intervals, which are of great interest for temperature and pressure retrieval from infrared atmospheric spectra, are still poorly modeled as demonstrated by a recent intercomparison of forward codes[a]. The model proposed is an extension of that proposed previously for the calculation of CO_2 Q branch line-mixing[b]. The Energy Corrected Sudden approach is used in order to build a relaxation matrix which takes into account the mixing of all the P, Q, and R lines in each vibrational CO_2 band, without any adjustable parameters. Comparisons of calculated spectra with a number of laboratory and atmospheric measurements have been made. High pressure absorption measurements were recorded in the 10–15 μm spectral interval for a CO_2 - N_2 mixture, in the 200–300 K temperature range. A large number of atmospheric spectra were also used, which were obtained with various experimental techniques and geometries of Earth observation. We used transmission measurements deduced from solar occultation recordings made with a ballon-borne (LPMA) and a ground-based (IMK) spectrometer. We also considered emission spectra recorded limb looking from a satellite (MIPAS) or a balloon (SAO) as well as air-borne measurements using Nadir geometry (HIS). In all cases the residuals between calculated and measured values are within experimental errors and good agreement is obtained in

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the regions of far wings of CO_2 bands where the Lorentzian line-shape model leads to considerable errors trough overestimation of the absorption.

EFFECT OF DENSITY AND TEMPERATURE ON THE INFRARED SPECTRA OF FLUID ETHENE BY MOLECULAR DYNAMICS SIMULATIONS

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A study of the influence of density and temperature on the dynamical behavior of ethene molecules in bulk liquid and gas phases is performed by classical molecular dynamic simulation technique. The simulations were carried out for the density of the system in the range from 600 to 900 $kg.m^{-3}$ and at 1.26 $kg.m^{-3}$ in the gas phase at 123K and for the temperature in the range from 73K to 203K at 750 $kg.m^{-3}$. The analysis of the infrared spectra shows strong modifications upon the increasing of the density and upon the temperature. Firstly, going from gas to liquid phase at the same temperature, the change in rotational motion of the molecules modifies the shape of the infrared bands and secondly, the frequencies of the bands shift upwards while the pressure increases in the liquid phase. Increasing the temperature, the shape of the spectrum changes, frequencies of the bands shift upwards and other downwards.

EXPERIMENTAL AND SIMULATED INFRARED SPECTROSCOPIC STUDIES OF THE INTERACTION OF ETHYLENE ON A MFI ZEOLITE

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The physisorption of organic compounds on MFI zeolites is usually described by type I isotherms but for the adsorption of tetrachloroethene or p-xylene, stepped-isotherms are observed at room temperature. Therefore, a lot of macroscopic (gravimetry, microcalorimetry) and microscopic (in situ XRD, in situ neutron diffraction, in situ FTIR) experimental techniques were used to understand the adsorption process of tetrachloroethene[1-4], a highly symmetric admolecule tightfit within the flexible micropore network of the zeolite. The in situ FTIR spectroscopy was one of the most sensitive techniques to underline modifications of both zeolite framework and state of the sorbed phase. In particular the dependence of the location and the intensity of the most significant framework and sorbate vibration bands on tetrachloroethene loading highlighted discontinuities at 4 and 6 molec.uc^{-1} which were only partially evidenced by using other experimental techniques. However, experimental FTIR data cannot be elucidated without simulation complementary studies. In the present study ethylene instead of tetrachloroethene, was chosen as highly symmetric adsorbate. Both experiments and molecular dynamics simulation are done under similar conditions. The model used for ethylene and for the MFI zeolite considering an initial Pnma orthorhombic structure[5] is a full atomic one. Both are flexible using the potential used by Jianfen et al.[6] for ethylene and for the interaction with the zeolite, and the potential proposed by Ermoshin et al.[7] for the intramolecular dynamic of MFI. Aggregates of 18 unit cells of zeolite with various loading of ethylene are simulated in contact with its gas at 300 K. IR spectra of ethylene, zeolite and ethylene adsorbed on zeolite are then calculated over equilibrium trajectories. Simulated FTIR spectra of a MFI zeolite interacting with ethylene are analyzed as a function

of loading and compared with the experimental results.

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DIPOLE MOMENT CALCULATIONS AND STARK EFFECT STUDIES IN THE LOW-LYING STATES OF RbCs

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Potential curves, permanent and transition dipole moment functions for the low-lying electronic states of the RbCs molecule in the framework of the Hund's "c" coupling scheme were computed using the relativistic shape-consistent pseudopotential model for inner atomic cores. The outer-core - valence correlation and outer-core polarization effects were evaluated by the second-order many-body multipartitioning perturbation theory (MPPT) for state-selective effective Hamiltonians[1]. The effective Hamiltonian eigenvalues provided the energy estimates for the electronic states under study; the corresponding eigenvectors were further used to compute transition dipole matrix elements via the construction of requisite spin-free one-body transition density matrices. The contributions to these matrices from outer-space determinants (and thus core-valence correlation effects on the transition dipoles) were calculated at the first order of the MPPT. The approach guaranteed the size consistency of energy and transition moment estimates and allowed us to properly reproduce the presence of the so-called "non-classical" (two-body) terms in the effective valence-shell dipole operator. It appears to be more adequate to describe the case of rather large amplitudes of spin-orbit interactions in the vicinity of the cesium atomic core. Then, the theoretical potentials and dipole moments were applied to estimate absorption Einstein's coefficients from the ground to first five excited ($\Omega = 1$) states arising from both singlet and triplet electronic states.

Stark effect was studied experimentally using Ar^+-laser excitation of the $(4)^1\Pi$ state correlating to the Rb(4d) + Cs(6s) atomic limit, with particular v, J values identified according to the data in paper[2]. The RbCs molecules were formed from a mixture of Rb and Cs metals in an alkali-resistant glass cell containing Stark plates with 1.5 mm gap. Emission intensity ratio of extra lines that appeared at dc electric field values up to 2 kV/cm has been measured with respect to the parent lines. Data processing[3] allowed determining the ratio of permanent electric dipole moment value over Lambda-splitting between different parity e/f components of a fixed J level.

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COMPARISON OF THE INSTANTON AND STANDARD WKB CONTRIBUTIONS TO TUNNELING SPLITTING SPECTRA OF FLOPPY MOLECULAR SYSTEMS

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Earlier[1-3], we have demonstrated the potentialities of the instanton method by calculating the tunneling splitting values of the ground vibrational level for the floppy molecules with two and three equivalent minima at their potential energy surface (PES). Some advantages of the application of the instanton method as compared to the standard quasiclassical (or WKB) approximation for describing the spectra of tunneling splitting of a floppy molecular system are proved.

In the present talk, we developed the instanton method for calculation of tunneling splitting values of the excited vibrational levels of the floppy molecules with two equivalent minima at their PES. We have obtained the following expression for the value ΔE_n of tunneling splitting of vibrational level with number n

$$\Delta E_n = 2\frac{\hbar}{\sqrt{\pi}}\frac{2^n}{n!\omega^{2n}}\left(\frac{K}{l_0}\right)^{2n+1} e^{-\frac{S_0}{\hbar}}. \qquad (1)$$

Here S_0 is the Euclidian action for the instanton trajectory $x_0(\tau)$, τ is an imaginary time, $l_0 = \sqrt{\frac{\hbar}{m\omega}}$ is the amplitude of the zero-point vibrations of the oscillator in a separate well, m is the reduced mass of oscillator and ω is its harmonic vibrational frequency. K is found from the asymptotic behaviour of the instanton solution $\dot{x}_0(\tau)|_{\tau\to\infty} \longrightarrow Ke^{-\omega\tau}$.

The influence of the PES anharmonicity on the tunneling splitting values was also studied. Taking into account the anharmonicity corrections γ_n in the energies of vibrational levels $E_n = \hbar\omega(n + 1/2 + \gamma_n)$ with $|\gamma_n| << 1$, we deduced the formula for tunneling splitting

$$\Delta E_n = 2\frac{\hbar}{\sqrt{\pi}}\frac{2^{n+\gamma_n}}{\Gamma(n+1+\gamma_n)\omega^{2(n+\gamma_n)}}\left(\frac{K}{l_0}\right)^{2(n+1/2+\gamma_n)} e^{-\frac{S_0}{\hbar}}. \qquad (2)$$

The tunneling splitting values calculated by the instanton method by formula (2) are equal to $\Delta E_0^{inst} = 0.81\ cm^{-1}$, $\Delta E_1^{inst} = 41.29\ cm^{-1}$ for two lowest levels of the vibration-inversion spectrum of the NH_3 molecule. The appropriate experimental and WKB values are $\Delta E_0^{exp} = 0.79\ cm^{-1}$, $\Delta E_1^{exp} = 35.84$

cm^{-1} and $\Delta E_0^{WKB} = 0.88\ cm^{-1}$, $\Delta E_1^{WKB} = 71.29\ cm^{-1}$, respectively. On the basis of the obtained results, we may conclude the principal advantage of the instanton method formulas in comparison with the the WKB ones, namely: the WKB approximation is based on the linear (Airy wave functions) connecting formulas, while the instanton method uses the harmonic oscillator wave functions for connecting formulas.

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ON THE DETERMINATION OF INTRAMOLECULAR POTENTIAL FUNCTION OF THE PH_3 MOLECULE

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The potential function of the PH_3 molecule is derived on the base of analysis of the band centers and rovibrational α_λ^β- coefficients of fundamental and first overtone and combination bands of the PH_2D species.
The analysis is also in progress, where the fit is fulfilled directly to the experimental transitions.

HIGH RESOLUTION FOURIER TRANSFORM SPECTRUM OF PD_3 IN THE REGION OF THE STRETCHING OVERTONE BANDS $2\nu_1$ AND $\nu_1 + \nu_3$

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The infrared spectrum of the PD_3 molecule has been measured in the region of the first stretching overtone bands on a Fourier transform spectrometer with a resoluton of 0.0068 cm^{-1} and analyzed for the first time. More than 800 transitions with $J^{max.} = 15$ have been assigned to the bands $2\nu_1$ and $\nu_1 + \nu_3$. An effective Hamiltonian was used which takes into account both the presence of resonance interactions between the states (2000) and (1010), and interactions of these with the third stretching vibrational state of the $v = 2$ polyad, (0020). A set of 44 spectroscopic parameters was obtained from the fit. This reproduces the 305 initial "experimental" upper ro-vibrational energies with an *rms* deviation of 0.0015 cm^{-1}.

Inspection of the assignment of the spectrum and furthermore the fit of the upper ro-vibrational energies allows one to draw conclusions about the closeness to the local mode limit of the PD_3 molecule in the (2000) and (1010) states. The analysis of the values of the band centers, Coriolis-type interaction parameters and vibrational anharmonic coefficients indicate that the local mode model is rather suitable for the description of the stretching ro-vibrational bands of PD_3.

OBSERVATION OF THE $\Delta v_{GeH} = 5$ STRETCHING VIBRATIONAL OVERTONE OF $H_3{}^{70}GeD$ BY ICLAS-VeCSEL TECHNIQUE. ROVIBRATIONAL ANALYSIS OF A PERTURBATION-FREE LOCAL MODE STATE

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The weak $\Delta v_{GeH} = 5$ stretching overtone transition of monoisotopic monodeuterogermane, $H_3{}^{70}GeD$, has been observed at high resolution by Intracavity Laser Absorption Spectroscopy (ICLAS) using a Vertical external Cavity Surface Emitting Laser (VeCSEL). The spectrum was recorded between 9750 and 9955 cm^{-1} at different pressures between 12 and 58 hPa in the intracavity cell. The generation time was set at 225 μs, which corresponds to an absorption equivalent path length of about 26 km.

The rotational analysis was performed in the frame of the traditional normal mode based theory. The analysis shows that the studied $v_{GeH} = 5$ level reveals perfect local mode behaviour for the (500, A_1) and (500, E) vibrational states up to high J. The fit of about 700 line positions reaches experimental precision, ca. 6×10^{-3} cm^{-1}, without requiring, up to J about 13, Coriolis interactions or any higher order terms: convergence was achieved refining only 8 free parameters (ν_s/ν_t, B_s/B_t, C_s/C_t, q_{eff} and α_{eff}^{BB}). Local mode relations ($\nu_s = \nu_t$, $\alpha_s = \alpha_t$, $q_{eff} = -\sqrt{2}\alpha^{BB}$) were found to be fulfilled within experimental precision. The parameters of the (n00, A_1/E) states, $n = 5$, are in excellent agreement with those of the previously analyzed $n = 2$, 3, 6, 7, and 8 states when their linear vibrational dependence is taken into account.

HIGH RESOLUTION STUDY OF SOME DOUBLY EXCITED VIBRATIONAL STATES OF PH_2D: THE $\nu_1 + \nu_2$, $\nu_2 + \nu_5$, $\nu_2 + \nu_3$, AND $\nu_2 + \nu_6$ BANDS

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High-resolution (0.0068 and 0.0038 cm^{-1}, respectively) Fourier transform spectra of the PH_2D molecule were recorded for the first time in the regions of the $\nu_1 + \nu_2/\nu_2 + \nu_5$ and $\nu_2 + \nu_6/\nu_2 + \nu_3$ bands. Altogether about 1450 measured transitions yielded 197, 154, and 191 upper state ro-vibrational energies of the (010001), (011000), and (110000) states, respectively. The 48 transitions caused by the resonance interactions and belonging to the weak $\nu_2 + \nu_5$ band have been also assigned. The upper energies were fitted using a Watson-type Hamiltonian (A reduction, III^l representation) taking into account resonance interactions. The derived set of parameters reproduces the ro-vibrational energy terms of the analyzed vibrational states with an *rms* deviation of 0.0007 cm^{-1}.

GLOBAL ANALYSIS OF CHLOROMETHANE : RECENT RESULTS INVOLVING THE REGION FROM 1900 to 2600 cm^{-1}

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As part of a global analyis of the infrared spectrum of chloromethane, recent results involving the region from 1900 to 2600 cm^{-1} will be reported. The first step of this study was the recording of high resolution Fourier transform spectra of pure $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ isotopomers and the simultaneous analysis of the lower four polyads of the molecules (0 to 1800 cm^{-1}) (1). The present work is devoted to the fifth polyad involving the upper states of seven interacting bands $2\nu_6$, $\nu_2+\nu_3$, $\nu_3+\nu_5$, $3\nu_3$, $\nu_2+\nu_6$, $\nu_5+\nu_6$, $2\nu_3+\nu_6$. The sixth order effective hamiltonian adapted to the polyad structure of the molecule contains 557 symmetry allowed terms (in irreducible tensor form) among which 209 are known from the prior analysis of the lower four polyads. More than 20 000 transitions for each isotopomer have been assigned and fitted with a standard deviation better than 4 10^{-4} cm^{-1} which is close to the experimental precison and represents an improvement of nearly two orders of magnitude with respect to previous works for the bands analyzed earlier. Furthermore, a precise account for local resonances within this region have provided accurate complementary data used to refine ground state constants that remained badly determined so far.

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THE ν_5 BAND OF CH_3CD_3: HIGH RESOLUTION SPECTRUM AND GLOBAL THREE-BAND ANALYSIS

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The lowest frequency parallel fundamental band ν_5 of CH_3CD_3 near 900 cm^{-1} was measured at low temperature with a resolution of 0.0021 cm^{-1} using Fourier transform spectroscopy. The band is weak, and an absorption path of 60m was used. Large torsional splittings due to inter-vibrational coupling have been observed. Building on previous studies of the torsional levels in the ground vibrational state and and in the methyl rocking state ($\nu_{12} = 1$), a three-band analysis including this most recent data has been completed. The combined data set of more than 2,200 frequencies was fitted to within experimental accuracy using a 43-term model Hamiltonian. The results were found to bear a striking resemblance to those of an earlier, analogous study of CH_3SiH_3. In both cases, Fermi coupling between the ($\nu_5 = 1$) state and the ground state was found to be the dominant interaction responsible for the observed torsional splittings. Inclusion of this coupling results in a simplification of the ground-state Hamiltonian, so that only eight additional terms were required with the introduction of the ν_5 band.

SUMMARY OF RECENT ANALYSES OF THE FIRST FOUR POLYADS OF METHANE

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In methane, interacting vibrational states are grouped into polyads which must be treated simultaneously. The energy levels of successive polyads are studied using an extrapolation method.

This poster presents the most recent results both for frequencies and intensities[a]. Today, we can consider that the polyads P_0 (ground state), P_1 (dyad), P_2 (pentad) and P_3 (octad) are well known, allowing a precise calculation of the corresponding hot bands. The results for the next polyads will be also shown.

The HITRAN[b] and STDS[c] databases have been updated recently according to these results.

[a]Part of the research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, Langley Research Center under contract with the National Aeronautics and Space Administration.

[b]`http://www.hitran.com`

[c]`http://www.u-bourgogne.fr/LPUB/sTDS.html`

DETAILED INVESTIGATION OF THE ICOSAD (1.3 – 1.5 μm) OF $^{12}CH_4$ AT HIGH-RESOLUTION: PRELIMINARY ANALYSIS OF THE $\nu_2 + 2\nu_3$ REGION

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Recent interests in high temperature methane spectra, especially in the astrophysical domain (atmospheres of brown dwarfs), has increased the need for reliable models and simulations for the various vibrational polyads of CH_4 at increasing energy. While the 0 – 4850 cm^{-1} region (ground state, dyad, pentad and octad) can be considered as well known[a], the tetradecad system (5000 – 6500 cm^{-1}, 14 interacting levels) is still under investigation[b,c].

Recently, high-resolution FTIR and cavity ring-down (CRD) spectra of the icosad (6600 – 7700 cm^{-1}, 20 interacting levels) have been recorded [d]. Due to the huge complexity of this polyad, its detailed analysis will be a difficult task. In this poster, we present a preliminary analysis of these new data, namely in the intense $\nu_2 + 2\nu_3$ region near 7500 cm^{-1}. This analysis has been realized thanks to the STDS program set[e]

`http://www.u-bourgogne.fr/LPUB/sTDS.html`

It has also benefited from a recent *ab initio* calculation that provided accurate positions for the vibrational sublevels[f].

The figure below shows a comparison between a jet-cooled CRD spectrum[d] of the $\nu_2 + 2\nu_3$ Q branch and the corresponding simulation. The results will be discussed in relation to full dimensional potential energy and electric dipole hypersurfaces [g].

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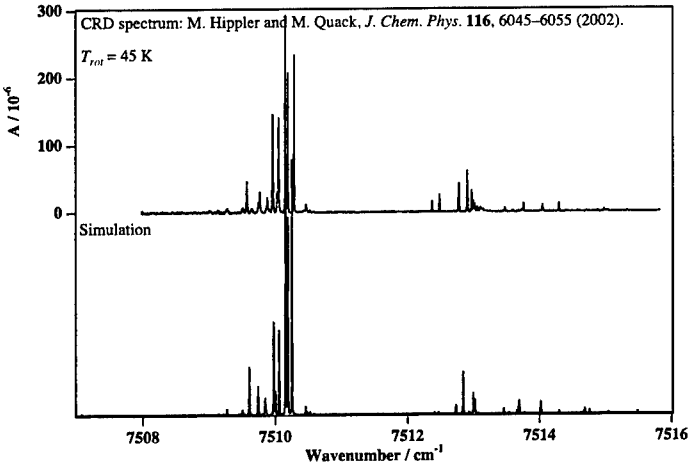
CRD spectrum: M. Hippler and M. Quack, J. Chem. Phys. 116, 6045–6055 (2002).
T_{rot} = 45 K
Simulation
A / 10^{-6}
300
200
100
0
7508
7510
7512
7514
7516
Wavenumber / cm^{-1}

HIGH RESOLUTION UV SPECTROSCOPY OF 4-DIMETHYLAMINOBENZONITRILE

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The molecule 4-dimethylaminobenzonitrile (DMABN) is studied extensively by many groups. Nevertheless, there are many questions left. For example: what is the geometrical structure in the electronic ground state and in the excited state? Furthermore, there is some confusion about the value of the life time of the excited state. Based on rotational band contour analysis, Saldago et al (JPC A 103 (1999) 3184) determined the life time of the various vibrational energy levels in the S_1 state to be in the picosecond range (1.5-24 ps). But other groups think that the life time is on the nanosecond time scale. Ultrahigh resolution laser induced fluorescence (LIF) spectroscopy is a powerful tool to obtain more detailed information on the geometrical structure and excited state lifetime of molecules. We have investigated two rovibronic bands of DMABN using UV LIF in combination with a molecular beam. Since the measured spectra show rotationally resolved transition, it is immediately clear that the life time is not in the picosecond range. A detailed analysis provides the rotational constants in the ground and the excited states.

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HIGH-RESOLUTION FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $C^4\Delta - X^4\Phi$ TRANSITION OF TiCl

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Visible spectroscopy of TiCl has been performed since long, but the complexity of its spectrum hampered obtention of unambiguous assignements. This is only recently that considerable experimental investigations in the infrared[a,b], visible[c], and submillimeter[d] ranges as well as accurate ab initio calculations[e,f,g,h] enabled correct definition of its low-lying electronic states.

Here, the emission spectrum of $Ti^{35}Cl$ around 3 μm has been recorded with a high resolution Fourier transform spectrometer. TiCl has been produced through a continuous flow of $TiCl_4$ vapor and helium excited in an ac discharge.

In the 0-0 (already investigated by Ram and Bernath[a]) and 1-1 bands of the $C^4\Delta - X^4\Phi$ transition, all the four spin components 1/2-3/2; 3/2-5/2; 5/2-7/2; 7/2-9/2 subbands have been observed, whereas only three subbands of the 2-2 transition (1/2-3/2; 5/2-7/2; 7/2-9/2) and the 7/2-9/2 subband

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of the 3-3 transition were found intense enough to be measured. For each observed subband, effective rotational parameters have been derived. Additionally, molecular constants of the $C^4\Delta, v{=}0$ and $C^4\Delta, v{=}1$ levels have been determined by performing a diagonalization of the Hamiltonian matrix. Moreover, a perturbation affecting the $C^4\Delta_{1/2}$ $v{=}0$, 1, 2 levels appears as arising both from Λ doubling and avoided crossing phenomena. Partially deperturbative treatment has been performed and confirms the existence of the $A^4\Sigma^-$ and $B^4\Pi$ states, which have only been predicted by ab initio calculations[f,h] so far.

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SASSI EXTRACTION OF UNDERLYING FEATURES IN HIGH RESOLUTION FTIR SPECTRA

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The analysis and assignment of the high resolution FTIR spectra of halogen and hydrogen substituted fluorocarbons such as CFC's, HCFC's, HFC's and FC's is essential for a full understanding of their spectra and in order to monitor these atmospherically important species. However even quite small molecules of this type usually have complicated overlapping spectral bands that are further congested with extensive rotational structure, hot bands and bands from several isotopomers. The rotational lines are also often perturbed by interactions with neighbouring states. We have developed an enclosive flow cell[1] based on the design of Bauerecker[2] in order to obtain "simplified" rotationally and vibrationally cold spectra and have recorded high resolution FTIR spectra of a number of species including perfluorocyclobutane, pentafluorethane, tetrafluoroethylene, Dichlorodifluoromethane, 1,1,1,2-tetrafluoroethane, chlorodifluoromethane and 1,1- difluoroethane. In this paper we will describe the enclosive flow method for obtaining supercooled spectra and compare the results with the method of supersonic jet expansion. Using Spectral Assignment by Subtraction of Simulated Intensities (SASSI), we will also show how it is possible to more fully assign the rotational structure of hot bands and less abundant isotopomers in both cooled spectra and room temperature spectra. Assignments of the ν_2/ν_7 and ν_3/ν_8 band systems of chlorodifluoromethane (HFC-22) will be presented to show the power of the combination of enclosive flow cooling and SASSI.

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Poster Session M

Thursday, September 11, 20:00

RIGID DIATOMIC MOLECULES IN A STRONG EXTERNAL FIELD

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The rotational motion of a molecule in an external field is a hindered rotation. In the case of weak fields a perturbation treatment based on free-rotor states can easily be used to evaluate the shifts in energy levels and transition moments. This is what is usually done, for instance, in Stark-effect calculations. However, when the field is strong, the rotational quantum number J is no longer a good quantum number and the energy levels can be better understood as vibrational states. In this case a free-rotor basis set becomes less appropriate. In the case of a strong Stark-effect such strongly-hindered states are referred to as "pendular states" [a]. It is not only in electric fields that aligned states can arise. Molecules adsorbed on a surface or trapped in a matrix can also experience alignment. In these cases a richer range of possibilities presents itself as the potential may have multiple minima.
By direct numerical solution of the Schroedinger equation we can calculate energy levels and transition moments of aligned states in an axial symmetric field of arbitrary strength. Here we present results in the form of correlation diagrams for the case of an external potential with two minima differing in energy and separated by a potential barrier.

[a]For example, J.M. Rost, J.C. Griffin, B. Friedrich, and D.R. Herschbach, Phys. Rev. Lett. 68, 1299 (1992); P.A. Block, E.J. Bohac, and R.E. Miller, Phys. Rev. Lett. 68, 1303 (1992).

KINETIC MODELING OF FEMTOSECOND DYNAMICS IN CURVE-CROSSING SYSTEMS

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Vibrational dynamics observed in femtosecond experiments is usually simulated in terms of quantum wave packet dynamics. In a simplified approach, wave packet evolution can be represented by a sequence of first-order reactions. Reagents and products of elementary steps are considered as transitions states in the course of nuclear dynamics [a].

In this work, we used the kinetic approach to simulate experimental and computational data on femtosecond dynamics in curve-crossing systems. We constructed the kinetic models for indirect dissociation of NaI and photo-induced isomerization of retinal, an important biomolecule. In both cases wave packet motion in the single electronic states was modeled by consecutive first-order reactions, whereas splitting of wave packet near the crossing region was represented by two competitive reactions. The rate constants of consecutive reactions were determined by the time of classical motion along the electronic term and the number of elementary reactions. The latter parameter was varied to achieve the better agreement with the experimental data. The rate constant ratio in competitive reactions was determined by the probability of adiabatic transition in the crossing region.

Solving the system of kinetic equations, we obtained the time-dependent population of transition states during NaI dissociation, and simulated the build-up of the product (atomic sodium) accumulation.

The kinetic model of retinal isomerization contains four branches, describing motion along two diabatic potentials, and two crossing regions. The kinetic populations of transition states and reaction product were compared to populations obtained by exact quantum-dynamical calculations. We showed that kinetic model gives qualitatively correct description of reaction dynamics up to three vibrational periods (about 700 fs).

This work was supported by Russian Foundation for Basic Research (Grant no. 03-03-32521).

[a] K. Moller and A. Zewail, *Chem. Phys. Lett.*, **351**, 281-288 (2002).

CONTROLLING ROTATIONAL DYNAMICS OF MOLECULES BY PHASE-SHAPED FEMTOSECOND LASER PULSES

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Coherent control of the rotational dynamics in N_2 molecules by means of pulse shaping technique is reported. In this work, a femtosecond laser pulse is used to produce a rotational wave packet in the ground state of N_2 via a stimulated Raman process. The laser pulse is tailored by a spatial light modulator allowing spectral phase modulation. By applying judicious phase modulations, the rotational structure of the wavepacket (both amplitude and phase) is accurately controlled and its temporal evolution, observed by a time-domain polarization technique, fully interpreted. Applications to optical diagnostics and molecular alignment by ultra-short laser pulses are discussed.

FEMTOSECOND DEGENERATE FOUR-WAVE MIXING (DFWM) AND COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (CARS) IN CO_2 AND H_2

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Two experimental methods have been applied to study rotational and vibrational Raman spectra of molecules in the time domain. Both methods make use of non-linear four-wave-mixing spectroscopy : time resolved degenerate four-wave mixing (DFWM) and coherent anti-Stokes Raman spectroscopy (CARS). The first relies on the coherent excitation of rotational states with femtosecond lasers. Two ultrashort pump pulses of wavelength λ, spatially and time overlapped, are crossed at a given angle in a gas sample. These two pulses produce a superposition state through stimulated Raman excitation. The superposition state then exhibits rotational quantum beats, which can be probed with a time delayed third pulse. The probe beam interacts with the pump beams in a folded BOXCARS beam geometry. The DFWM signal, of wavelength λ, is generated in the direction of phase matching and recorded by a photomultiplier as a function of the time delay. In the CARS experiment, the same interaction geometry is kept and the only difference is the use of two wavelengths for the excitation process. These wavelengths are chosen to excite a vibrational band of the molecule. Therefore, rotational coherences are produced between the vibrational states. Both experiments are based on a chirped pulsed amplified Ti:Sapphire femtosecond laser delivering pulses of 90 fs duration. The three beams for the DFWM setup are all derived from the laser system at 800 nm. For the CARS experiment, a part of the 800 nm output is frequency doubled and used to pump a non-collinear optical parametric amplifier (NOPA) operating in the visible. The output of the NOPA is split into two parts to produce one of the pump pulses and the time delayed probe pulse. Preliminary results have been obtained with the two techniques. =46irst, DFWM experiments conducted in CO_2 gas have been interpreted in terms of alignment of the molecule. Second, CARS spectroscopy has been performed in pure H_2 and H_2-N_2 mixtures with at high pressure and high temperature. The effects of collisional relaxation on the CARS traces will be discussed and the measurement of collisional parameters will be presented.

ADIABATIC RAPID PASSAGE AND OTHER NONLINEAR SPECTROSCOPIC EFFECTS IN THE SPECTRA OF NITRIC OXIDE AND METHANE AT 5 μm

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Following rapid passage experiments by McCulloch, Duxbury and Langford using a pulsed down-chirp quantum cascade laser spectrometer, we have extended the method by utilizing a novel system in which short red or blue frequency chirped pulses can applied to specific molecular velocity classes across a Doppler broadened molecular absorption line. The output from the QCL passes through an astigmatic Herriott cell with an effective path length of approximately 100 m. The molecules studied in this way have been nitric oxide and methane. We will describe a variety of nonlinear optical phenomena which can be explored in this way, including adiabatic following and the Autler-Townes effect. The relationship between this selective probing of specific velocity groups of the Doppler broadened lines and the adiabatic passage experiments involving all velocity components will be described.

RAPID PASSAGE AND POWER SATURATION EFFECTS IN PULSED QUANTUM CASCADE LASER SPECTROMETERS

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Recently there has been considerable interest in adiabatic passage effects in atomic and molecular gases subject to short laser pulses. In the infrared region the relation times of low pressure molecular gases are on the microsecond time scale. In our experiment the time of passage of the chirped QCL pulse through a Doppler broadened line is sub-ns, very much faster than in earlier experiments, greatly enhancing the chance of seeing rapid passage effects. Since the intensity of the pulse is about, 104 W m^{-2}, the combination of high intensity and a short interaction time, which is much faster than the relaxation processes, leads to the observation of strong adiabatic rapid passage signals and power dependent bleaching. We have observed these effects in several gases, in particular ethylene, methyl chloride and ammonia. Examples are given of the effects of the short interaction time and power bleaching on the observed spectral profiles of lines, even when pressure broadened with up to 100 Torr of nitrogen. Although only three molecular examples are considered in detail, we will show that these effects are present when any short, intense QCL pulse is used to probe the spectrum of specific molecules such as ethylene, irrespective of the mode of operation of the spectrometer.

CONTROLLING THE MOTION OF HYDROGEN MOLECULES

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Recent experimental results will be described in which hydrogen molecules are excited to Rydberg states and inhomogeneous electric fields are applied to control the translational motion. The aim of this work is to produce bunches of Rydberg molecules with narrow velocity distribution (and hence well-defined distribution of wavelengths) so that highly controlled reactive and inelastic scattering experiments can be performed, to permit spatial separation of molecules in different quantum states, and to achieve molecular cooling and trapping. The work in our group is closely related to the experiments of Meijer et al [a] in which highly polar ground-state molecules have been trapped at low temperatures (20 mK) by deceleration in a sequence of inhomogeneous electric field stages. The general principle applied in both sets of experiments is that a molecule in a low-field seeking state (one whose energy increases with increasing field) experiences a repulsive force in a direction away from a high field region of an electrostatic dipole. Our approach [b c d] takes advantage of the high polarizability of a Rydberg electron orbital, and the linear 1st order Stark effect in the high-l Rydberg states. By spectroscopic selection of an appropriate eigenstate in the presence of an electric field, it is possible to create a very large dipole moment exceeding the dipole moments of ground-state molecules by many orders of magnitude. In this way a much larger decelerating force can be achieved using more modest electric fields; typically we use no more than 1000 V/cm.

Rydberg states of H_2 are selected by two-photon, two-color excitation (VUV + UV) proceeding via a selected rotational level ($J = 1$) of the $B^1\Sigma_u^+$ intermediate state. The Stark map showing how the energy levels vary with electric field is determined by recording Rydberg excitation spectra for a range of fields and simulating these by diagonalising the effective Hamiltonian in an appropriate basis set.

[a] H. L. Bethlem, F. M. H. Crompvoerts, R. T. Jongma, J. Y. T. van de Meerakker and G. Meijer, Phys. Rev. A, 65 (2002) 053416.

[b] A. L. Goodgame and T. P. Softley, J. Phys. B., 32 (1999) 4839

[c] D. Townsend, A. L. Goodgame, S. R. Procter, S. R. Mackenzie and T. P. Softley, J. Phys. B., 34 (2001) 439

[d] S. R. Procter, Y. Yamakita, and T.P. Softley, Chem. Phys. Lett., In Press (2003)

The molecules are then exposed to the inhomogeneous field of an electric dipole for a fixed period of time ($\sim \mu$s), and their trajectories are monitored by field ionization and ion imaging or time of flight measurement. With the dipole oriented parallel to the molecular beam direction, the molecules are deflected out of the main beam path, whereas with the dipole oriented perpendicular, deceleration or acceleration is observed. Surprisingly, if the field-ionization pulse is not applied and the Rydberg molecules are allowed to fly all the way to the detector before ionization, a flight time of 110 μs, sufficient Rydberg molecules survive for this length of time to be detected. The observed deflections and decelerations are in agreement with those predicted in classical trajectory simulations. Simulations will be presented for a proposed setup to decelerate the molecules to zero velocity and trap them.

A COBRA FT-MW SPECTROMETER WITH COAXIALLY ALLIGNED ELECTRODES FOR STARK-EFFECT APPLIED IN RESONATORS (CAESAR)

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We present a novel setup for Stark-effect measurements using a Fourier transform-microwave (FT-MW) spectrometer with coaxially oriented beam-resonator arrangement (COBRA). Up to now parallel plate electrodes are used in pulsed supersonic jet expansion FT-MW spectrometers for Stark-effect measurements. To avoid line broadening by an inhomogeneous field or even signals from zero-field regions, the valve is normally mounted above the electrodes and not behind one of the reflectors, i.e. a supersonic expansion perpendicular rather than parallel to the resonator axis is used. Thus, sections of the jet which are in inhomogenous regions of the static electric field are also outside the resonator field, i.e. are kept away from effective polarization and sensitive detection. Broadened and zero-field lines are suppressed, but on the expense of the sensitity and resolution provided by the coaxial beam-resonator arrangement. Some recent developments address the disadvantages in different ways[ab], but maintain the conventional parallel plate approach.

The open Fabry-Perot type arrangement of spherical mirrors provides the possibility to mount the reflectors electrically insulated. Since no electrical surface currents of the resonator are inhibited, the propagation of the microwave field remains unaffected. If the microwave antennas and the valve are mounted at the same mirror, the other reflector can be set to a static HV potential. Together with a number of coaxially arranged circular electrodes a homogeneous field along the resonator axis can be achieved, allowing accurate Stark-effect measurements with COBRA FT-MW spectrometers. The arrangement is suitable even at low frequencies, where the microwave field occupies a large volume for propagation in one of its gaussian modes, i.e. a parallel plate arrangement would severely interfer with the microwave field. The experimental setup along with electrostatic calculations for the geometry will be presented. The performance of the new Stark-effect arrangement will be demonstrated by spectral examples.

[a]Z. Kisiel, J. Kosarzewski, B.A. Pietrewicz, and L. Pszczolkowski, Chem. Phys. Lett. 325, 523(2000).

[b]D. Consalvo, Rev. Sci. Instrum. 69, 3136(1998).

VIBRATIONAL ENERGY LEVELS AND POTENTIAL ENERGY SURFACE OF METHYL FLUORIDE

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Variational methods are presented for the calculation of excited stretching and (separately) bending vibrational states of centrally connected, C_{3v} pentaatomic molecules. The use of polyspherical coordinates simplifies the derivation, form and application of the exact kinetic energy operator and importantly also facilitates exploitation of the full C_{3v} symmetry. A direct product FBR basis is used for both the stretching and bending calculations. In the bending calculation a series of basis set contractions in each coordinate are performed. The code does not assume any particular functional form for the potential energy surface, requiring the use of multi dimensional numerical integration. Separate stretching (four dimensional) and bending (five dimensional) potential energy surfaces have been determined for CH_3F by fitting to 3500 *ab initio* points calculated at the CCSD(T) level. Pure stretching and pure bending excited vibrational levels are presented. These states will be used as contracted basis functions in the solution of the fully coupled stretch-bend calculation which will ultimately resolve problems of assignment and interpretation of the infrared and near infrared overtone spectra of CH_3F.

LONG RANGE INTERACTION IN CALCIUM DIMER

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Recent progress in the development of a calcium optical frequency standard using the $(4p4s)^3P_1$ (m_j=0) $\rightarrow$ $4s4s^1S_0$ calcium's intercombination line has motivate us to perform a systematic study of the long range interactions between two calcium atoms. The main factor which limits the precision of the measurement of the clock frequency is binary collisions. For a reliable description of these processes we have undertaken a study of the shape of the potential energy curve describing the interaction between two ^1S Ca atoms by measuring the positions of rovibrational levels of the $X^1\Sigma_g^+$ ground state in the Ca_2 molecule. High resolution Fourier transform spectroscopy allowed us to accurately describe more than 99.8 % of the $X^1\Sigma_g^+$ state potential well [1]. In order to collect information about the position of the last bound levels of the ground state we have applied the filtered laser excitation technique. Transition frequencies of the Ca_2 B-X system from asymptotic levels of the $X^1\Sigma_g^+$ ground state reaching $v'' = 38$ were measured. The highest observed level is only 0.2 cm^{-1} below the molecular $^1S+^1S$ asymptote and has an outer classical turning point of about 20 Å. The extraction of confidence limits for the value of the long range coefficients C_6, C_8, C_{10} and the dissociation energy from the experimental data involving Monte Carlo simulation was implemented. A range for the s-wave scattering length has been derived as well [2].

The description of the collision involved during the laser interrogation of the intercombination transition necessitates also a precise knowledge on the $c^3\Pi_u$ molecular state correlated to the $^3P_1 + {}^1S_0$ asymptote. This state has no dipole allowed transition to the ground state but is coupled to the $A^1\Sigma_u^+$ by the spin-orbit interaction. A single laser spectroscopy of the A state extended by the observation of induced collision satelites has been realised and perturbations due to the $c^3\Pi_u$ have been observed. A deperturbation analysis on the observed data has been realised using the Fourier grid Hamiltonian method describe in [3]. Potential energy curves of both states and the spin-orbit coupling have been derived. This preliminary study will allow an investigation on the $c^3\Pi_u$ asymptote by Doppler free spectroscopy in a molecular beam of Ca_2 and provide already access to the triplet manifold in calcium dimer.

[1] O. allard, A. Pashov, H. Knöckel and E. Tiemann, Phys. Rev. A, 66, 042503 (2002)
[2] O. allard, C. Samuelis, A. Pashov, H. Knöckel and E. Tiemann, accepted to EPJD
[3] C. Lisdat, O. Dulieu, H. Knöckel and E. Tiemann, Eur. Phys. J. D, 17, 319-328 (2001)

NEW EQUILIBRIUM PARAMETERS OF THE CO^+ MOLECULE: THE FIRST-NEGATIVE BAND SYSTEM ANALYSIS

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The presented paper shows results of our further researches of the emission spectrum of the $^{12}C^{16}O^+$molecule, a part of them has been presented in our previous work[a]. The $B^2\Sigma^+$ and $X^2\Sigma^+$ states of the have been investigated on the basis the First-Negative band system observation. Twenty two bands consists of the $0-v'', 1-v'', 2-v'', 3-v'', 4-v''$, 5-$v''$ progressions and 6-10 band were recorded in the high resolution conditions. The conventional technique of spectroscopy has been implemented.

Individual rotational analysis of the bands was performed via a nonlinear least-squares procedure and by using effective Hamiltonians of Brown *et al* [b]. Matrix elements of these Hamiltonians, definition of molecular constants and their physical meaning can be found in a paper by Amiot *et al* [c]. In this way each vibrational level of the $B^2\Sigma^+$ $(v = 0-6)$ and $X^2\Sigma^+$ $(v = 0-10)$ states has been described by the B_v, D_v, γ_v molecular constants. Also the $\nu_{v'-v''}$ band origins values have been calculated, for all observed bands.

All these constants have been used as a input data for the global merge calculus, giving single-value estimates of the molecular parameters for each vibrational level.

Equilibrium structure parameters have been determined for both considered states of CO^+, on the basis final merged constants, and using their $(v+\frac{1}{2})$ dependence. The many of them, especially for $B^2\Sigma^+$ state, have been determined for the first time.

Next the:

- vibronical term values for $(v' = 0-6)$ and $(v'' = 0-10)$,
- RKR-potential curves for $B^2\Sigma^+$ and $X^2\Sigma^+$ states,
- Franck-Condon factors and r-centroids for the First-Negative bands, have been calculated.

[a]Kępa R, Szajna W and Zachwieja M 2003 *J. Phys.B: At. Mol. Opt. Phys.*- submitted for publication

[b]Brown J M, Colbourn E A, Watson J K G and Wayne F D 1979 *J. Mol.Spectrosc.* **74** 294-318

[c]Amiot C, Maillard J P and Chauville J 1981 *J. Mol.Spectrosc.* **87** 196-218

This type of a global fit, for the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system, of the CO^+ molecule has been attempted for the first time.

ROTATIONAL SPECTRA AND MOLECULAR FORCE FIELD OF TRANS-1-CHLORO-2-FLUOROETHENE

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The millimeter-wave spectra of the $CH^{35}Cl{=}CHF$ and $CH^{37}Cl{=}CHF$ isotopomers, in natural abundance, have been observed for the first time. The experimental investigation has been largely supported by highly accurate theoretical predictions of the equilibrium structure, dipole moment, chlorine quadrupolar tensor and harmonic force field, previously carried out by the same authors.

Many $\Delta J{=}0,\pm1$ $\Delta K_{-1}{=}+1$ transitions for $CH^{35}Cl{=}CHF$ and $\Delta J{=}0$ $\Delta K_{-1}{=}+1$ transitions for $CH^{37}Cl{=}CHF$ have been detected and assigned. This allowed us to accurately determine the ground state rotational constants, quartic and some sextic centrifugal distortion constants, and nuclear quadrupole coupling constants for both ^{35}Cl and ^{37}Cl species.

As far as *ab initio* computations are concerned, the complete set of cubic (219) and quartic (780) force constants have been evaluated, in the internal coordinate space, by numerical differentiation of the analytic second derivatives determined using the second order Møller-Plesset many-body perturbation theory, MP2.

Experimental and computational details will be given.

THE EMPIRICAL EQULIBRIUM STRUCTURE OF TRANS-GLYOXAL FROM EXPERIMENTAL ROTATIONAL CONSTANTS AND CALCULATED VIBRATION-ROTATION INTERACTION CONSTANTS

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An ultimate goal of many high-resolution spectroscopic studies of molecules in the gas phase as well as many ab initio quantum chemical calculations is to obtain the molecular equilibrium structure. By combining experimental ground state rotational constants and vibration-rotation interaction constants calculated at a high level of theory, an accurate structure, the socalled empirical equilibrium structure, may be determined for a molecule as discussed in Ref. (1).

In the present work we consider the empirical structure of glyoxal, $C_2H_2O_2$, which is a planar molecule that exists predominantly in the trans-conformation. A total of nine high-resolution FTIR spectra of glyoxal, glyoxal-d_1, glyoxal-d_2 and glyoxal-$13C_2$ have been recorded with a resolution ranging from 0.003 to 0.004 cm$-$1. By means of simultaneous ground state combination difference analysis for each of these isotopologues using the Watson Hamiltonian improved ground state rotational constants have been obtained. The empirical equilibrium structure for trans-glyoxal has been determined using the ground state rotational constants B and C obtained for these four species, and vibration-rotation interaction constants calculated at CCSD(T)/cc-pVTZ level of theory.

A least squares fit of eight equilibrium rotational constants gives the following empirical equilibrium geometric parameters of trans-glyoxal. Three distances (in pm) r(C-C): 151.453(38), r(C-H):110.071(26), r(C-O):120.450(27). Two angles (in degrees) alpha(CCH): 115.251(24), alpha(HCO): 123.472(19).

(1) F. Pawlowski, P. Jørgensen, J. Olsen, F. Hegelund, T. Helgaker, J. Gauss, K. L. Bak and J. F. Stanton, J. Chem. Phys. 116,6482-6496(2002).

VARIATIONAL ENERGY OF THE GROUND STATE FOR ISOTOPIC MODIFICATIONS OF H_2^+

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An approach is based on the hamiltonian in the principal axes of inertia[a] written in Radau[b] coordinates. The keypoints of the approach are as follows:

- the Born – Oppenheimer approximation is not used. None of interparticle distance is fixed.
- eigenfunctions obtained as exact solutions of the suitably chosen zero-order Schrödinger equation[c] are the prototype of variational wavefunctions.

The Rayleigh – Ritz variational principle requires the minimum for the functional $E = min\frac{<\Psi|H|\Psi>}{<\Psi|\Psi>}$, here H – the Hamiltonian of a system, Ψ – a basis function. For a three-particle system[c] the function Ψ is represented as the product $\Psi = \Psi(\rho)\Psi(z)\Psi(t)$, where

$$\Psi(\rho) = e^{-\lambda_1\rho/2}\rho^{\lambda_2/2}L_n^{(\lambda_3)}, \quad \Psi(z) = (1-z^2)^{\lambda_4/2-1/4}C_m^{(\lambda_5)}(z),$$

$$\Psi(t) = (1-t^2)^{\lambda_6/2-1/4}C_l^{(\lambda_7)}(t),$$

$L_n^{(\lambda_2)}(\rho)$ being generalized Laguerre polinomials, $C_m^{(\lambda_5)}(z)$ and $C_l^{(\lambda_6)}(t)$ – Gegenbauer polinomials, λ_i ($i = 1, 2, \ldots, 7$) – variational parameters. For the ground state ($|\Psi> \equiv |0>$) non-zero matrix elements of the Hamiltonian $H =$ –

[a] A. Ya. Tsaune, J. Math. Chem. **29**, 97 (2001).

[b] R. Radau, Ann. Sci. École Normale Supérior **5**, 311 (1868).

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$\frac{\hbar^2}{2}\sum_{i=1}^{4} H_i + U$ (U – the Coulomb potential of the system) are

$$
\begin{aligned}
< 0|H_1|0 > &= \frac{1}{2}\left(\frac{1}{m_1}+\frac{1}{m_2}\right) < 0|\frac{1}{\rho}\frac{\partial^2}{\partial\rho^2}\rho|0 >, \\
< 0|H_2|0 > &= \left[-\frac{1}{2}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)+\frac{1}{m_1 m_2} < 0|F_1(z)|0 >\right] < 0|\frac{1}{\rho}\frac{\partial}{\partial\rho}|0 >, \\
< 0|H_3|0 > &= < 0|\frac{2}{\rho^2}|0 > \left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right) < 0|\frac{\partial}{\partial z}(1-z^2)\frac{\partial}{\partial z}|0 > \right. \\
&- \frac{1}{m_1} < 0|(1-z)\frac{\partial}{\partial z}|0 > + \frac{1}{m_2} < 0|(1+z)\frac{\partial}{\partial z}|0 > \\
&+ \left.\frac{1}{m_1 m_2} < 0|F_2(z)|0 >\right], \\
< 0|H_4|0 > &= < 0|\frac{2}{\rho^2}|0 > \left[\frac{1}{m_1} < 0|\frac{1}{1+z}|0 > + \frac{1}{m_2} < 0|\frac{1}{1-z}|0 >\right] \\
&< 0|(1-t^2)\frac{\partial^2}{\partial t^2} - t\frac{\partial}{\partial t}|0 >,
\end{aligned}
$$

where $F_1(z)$, $F_2(z)$ are functions of z. Matrix elements $< 0|F_1(z)|0 >$, $< 0|F_2(z)|0 >$ and $< 0|U|0 >$ are calculated numerically, the others – analytically. Calculation results will be presented in communication.

FOURIER TRANSFORM ABSORPTION SPECTROSCOPY OF HOD IN THE VISIBLE AND NEAR-INFRARED SPECTRAL REGIONS

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Fourier transform absorption spectra of H_2O and D_2O mixtures were recorded at high resolution (0.06 cm^{-1}) on a very long absorption path (600 meters). The HDO lines were identified in the spectra by carefully removing all H_2O lines, relying on our earlier results for the main isotopomer. This poster presents an extensive listing of the HDO lines in the visible and near-infrared spectral region (20000–11000 cm^{-1}). The line positions and absorption cross-sections are provided for all lines and compared to existing literature data. Preliminary measurements of the N_2-broadened HDO lines are shown.

FURTHER ANALYSIS OF THE NEAR INFRARED AND VISIBLE EMISSION SPECTRUM OF H_2

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Non adiabatic ab-initio calculations[a], multichannel quantum defect theory[b] and XUV multi-resonance experiments[c] have provided in the last decade a large amount of results on the energy level structure of H_2. These new data can be used to progress with the analysis of the emission spectrum of this molecule where a large number of lines remain unassigned[d,e]. In order to improve the rotational analysis and to observe new energy levels (which hopefully will be used in future calculations), we have decided to record and to analyse the emission spectrum of H_2 from several excitation sources and over a large spectral range (2000-25000 cm^{-1}) by means of Fourier Transform emission spectroscopy. Some of our first results showing the interest of this investigation will be presented and discussed.

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WATER LINE PARAMETERS IN THE NEAR INFRARED AND VISIBLE

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Previously recorded water vapour and water-air spectra have been analyzed[a] [b] [c] using newly developed spectroscopic software GOBLIN. An absorption room temperature long pathlength pure water spectrum recorded by Schermaul *et al* [d] has been fitted in order to otain line parameters for weak lines in the region 9000 – 12 700 cm^{-1}. This produced nearly 8000 lines belonging to $H_2{}^{16}O$, $H_2{}^{18}O$, and $H_2{}^{17}O$ water isotopomers. Line positions and intensities for 6600 weak lines have been derived. More then 1000 of them have not been previously observed. Comparison with other studies in this region when available gave a good agreement.

After identifying lines due to $H_2{}^{18}O$ and $H_2{}^{17}O$ transitions the spectrum was analysed using a variational line list calculated with program DVR3D[e]. A total of 7150 lines were assigned resulting in 338 new vibration-rotation energy levels for $H_2{}^{16}O$.

The pure water and water-air mixture spectra recorded by by Schermaul *et al*[f] have been fitted simultaneously to obtain a set of line parameters for water strong lines in the range 10150 – 11200 cm^{-1}. The results have been compared with the data from HITRAN data base which have been recently updated by Brown *et al*[g]

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FOURIER TRANSFORM ABSORPTION SPECTROSCOPY OF WATER VAPOUR IN THE VISIBLE AND NEAR INFRARED SPECTRAL REGIONS

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Water vapour absorption spectra were obtained by combining a high-resolution Fourier transform spectrometer with a long-path absorption cell, thus allowing the observation of very weak, previously unobserved, lines. The spectra were recorded from the near ultraviolet to the near infrared, at either 0.03 or 0.06 cm^{-1} resolution, under different pressure and temperature conditions. More than 16000 lines have been studied between 26000 and 9250 cm^{-1}. Their positions and intensities have been determined, and for many lines, self- and air-broadening coefficients, as well as pressure-induced shifts were obtained.[a] These parameters provide an extended and homogeneous dataset for water vapour, which is notably shown to significantly improve the HITRAN 2000 database[b] for atmospheric applications in the visible spectral region.[c] In this poster a preliminary analysis of the dependence of the broadenings and shifts with vibrational and rotational quantum numbers is given, as well as preliminary results regarding the temperature dependence of the water vapour line parameters in the near-infrared spectral region.

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HIGH-RESOLUTION VIBRATIONAL SPECTROSCOPY USING LASER DIFFERENCE-FREQUENCY SPECTROMETER

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A continuous-wave (cw) high-resolution mid-infrared spectrometer has been developed based on difference-frequency generation (DFG) by mixing two cw autoscanned Ti:Sapphire lasers in a GaSe crystal. The DFG spectrometer is continuously tunable in the wide spectral region of 8-20 μm without any "mode hop", with a linewidth of $\sim$ 1 MHz.
DFG spectra of various volatile organic compounds, such as acetylene (C2H2), ethylene (C2H4), benzene (C6H6), and toluene (C7H8) are investigated over the wavelength range from 10 to 15 μm with a resolution of $\sim 10^{-3}$ cm^{-1}.
The present work is aimed at study of line parameters (like line position, line strength and line broadening coefficient) and its application to quantitative analysis of heavy molecules in the gas phase by laser vibrational absorption spectroscopy.

ROVIBRATIONAL ANALYSIS OF THE ν_1 BAND OF CF_3Cl FROM SUPERSONIC SLIT JET DIODE LASER SPECTRA

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Chlorofluorocarbons (CFCs) have been widely used in the past decades as refrigerants, solvents in cleaners, blowing agents in the production of foam and propellants in aerosols, and their diffusion into the stratosphere gave rise to well studied severe environmental effects. Their UV photolysis releases chlorine atoms which heavily destroy the protective ozone layer. Infrared spectroscopy is a very powerful method for detecting these compounds and monitoring their temporal trends; the spectroscopic parameters obtained from high resolution spectra are necessary to take full advantage of the sensitivity of this technique. Among the different CFCs, chlorotrifluoromethane (CFC-13) is a very interesting compound and the spectral region around 1108 cm^{-1} is characterized by a strong absorption originated by the ν_1 fundamental. The high resolution infrared spectra reveal a very dense rotational structure with the simultaneous presence of transitions due to chlorine isotopomers and hot bands. We have recorded the diode laser spectra of this band in a supersonic slit jet expansion achieving a rotational temperature of about 50 K with a FWHM which in many cases is about 0.0007 cm^{-1}. These conditions allowed us to well resolve the K substructure in the P(J) and R(J) clusters and to discover in the Q-branch the two bandheads of ^{35}Cl and ^{37}Cl isotopic species. The least-squares fit of the assigned unblended lines provided a reliable set of accurate parameters for the $v_1 = 1$ state of both chlorine isotopomers. Details of the spectra and results from the analysis will be presented.

PYROLYSIS OF DEUTERATED PYRIDINE AND PCl_3: THE MILLIMETER-WAVE SPECTRUM OF DC_5N

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Gas-phase copyrolysis of pyridine and phosphorus trichloride produces large amounts of HC_5N in a flow system at 1200 °C. Using a commercial sample of fully deuterated pyridine it has been possible to produce DC_5N, whose rotational spectrum has been investigated in the millimeter-wave region for the ground state and for 13 vibrationally excited states which approximately lie below 650 cm^{-1}, namely $(v_6v_7v_8v_9v_{10}v_{11})$ = (000001), (000010), (000100), (001000), (010000), (100000), (000002), (000020), (000003), (000011), (000101), (001001), and (010001). Transition frequencies up to 457 GHz ($J = 180 \leftarrow 179$) have been measured for the ground-state spectrum, making the evaluation of the sextic distortion constant possible. The anharmonic resonances which couple the (100000) stretching state with the (000020), (001001), and (010001) bending states, and the l-type resonances which occur between the different sublevels of a given bending state have been taken into account in the analysis of the spectra, which yielded determinations of the α_6, α_7, α_8, α_9, α_{10}, and α_{11} vibration-rotation coupling constants, and of the $x_{L(11,11)}$, $x_{L(10,10)}$, $x_{L(10,11)}$, $x_{L(9,11)}$, $x_{L(8,11)}$ and $x_{L(7,11)}$ anharmonicity constants.

ROVIBRONIC STATES OF HCN

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One of the major activities at the molecular spectroscopic laboratory of the Justus-Liebig University in the last years was the high resolution spectroscopy of HCN and HNC molecules. In the period of 1993-1997 about 80 high resolution absorption spectra have been recorded in the range of 300-12000 cm^{-1} with a pathlength up to 400 m [1-4]. Later, a very sensitive emission apparatus for the Bruker IFS 120 HR high resolution FT-IR spectrometer was constructed. Using this apparatus many very highly excited vibrational states of these molecules and their isotopomers were characterized for the first time [5-9].

This work is a continuation of the high resolution infrared emissions spectroscopy of HCN and reports the analysis of further 66 bands. 30 rovibronic states of HCN as e.g. 28^80 at 12603 cm^{-1} could be characterized for the first time and for 25 states it was possible to improve substantially the existing constants.

For the analysis of the very dense emission spectra with many overlapping features the development of a new spectrum analysis software was necessary. The software executes a combined lineshape analysis and transition wavenumber fit to matrix element parameters. The software manages a dynamic link between line positions and assignment data. Using this technique the lineshape analysis can be improved using the information from the calculated wavenumbers of the already assigned bands without a reassignment of the improved lineposition list. Examples for this analysis technique will be presented.

Up to now there are spectroscopic constants for 190 rovibronic states of HCN, not less than 102 states were observed at Giessen in emission and used for the characterization of these states.

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ON THE GLOBAL QUANTUM NUMBERS IN THE HCN↔CNH MOLECULE

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After discussing the concepts of local and global classical actions and corresponding quantum numbers, we introduce and analyze a model system based on a deformation of a spherical pendulum that can be used to reproduce large amplitude bending vibrations of floppy triatomic molecules with two stable linear equilibria. We apply the same analysis to the HCN molecule using the recent vibrational potential by Tennyson *at al* in [J. Chem. Phys. **115**, 3706 (2001)]. We find that contrary to our model system, global quantum numbers can be introduced for HCN↔CNH at all energies where the potential is expected to work.

SEMIEMPIRIC APPROACH FOR CALCULATION OF H_2O AND CO_2 LINE BROADENING AND SHIFTING

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To calculate line broadening and shifting induced by pressure of different buffer gases the impact theory has been modified on the wider use of empiric data by introducing of the additional parameters taking into account the trajectory bending, effects of vibrational excitation, corrections to the scattering matrix obtained from the perturbation theory, etc. Model parameters were determined by fitting the broadening coefficients to experimental data. This allows sufficiently accurate prediction of the parameters of line profiles, which were not measured. J-dependence of line shift coefficients for water (010)-(000) band (R-branch) lines induced by N_2 pressure in a wide range of J quantum numbers up to 18 was analyzed by authors recently. Here we continue this study for line broadening coefficient. According to developed approach the numerous calculations were performed, which allow to conclude about more complicated rotational dependence of broadening coefficient than it was considered before. The coefficients of CO_2 spectral lines broadening and shifting by air and nitrogen pressure are presented, as well as the coefficients of thermal dependence of line profiles. The calculated parameters are intended for use in spectroscopic databases. The calculations of the oxygen, nitrogen and argon pressure - induced shift coefficients for more than 100 water vapor absorption lines in the spectral region 5000 - 5560cm^{-1} have been performed. Calculations are in satisfactory agreements with experimental data. The shifts of the same lines induced by pressure of different buffer gases were compared, and the roles of different terms of the intermolecular potential in the formation of line shifts were studied. The coefficients of CO_2 spectral lines broadening and shifting by air and nitrogen pressure are presented, as well as the coefficients of thermal dependence of line profiles. The calculated parameters are intended for use in spectroscopic databases. The authors acknowledge the support by the Russian Foundation of Fundamental Research (grant N 02-07-90139 and N 01-05-22002) and Ministry of Education (grant N E02-3.2-91).

INVESTIGATION OF THE ROTATION-VIBRATION OF H_2O ISOLATED IN SOLID RARE GASES. NUCLEAR SPIN CONVERSION AND MATRIX EFFECT

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Water is a key molecule for the chemistry of the atmosphere and interstellar medium. Many studies have been devoted to chemistry involving this molecule and in particular to its ability to form weakly bonded complexes with molecules of astrophysical interest.

The water molecule is known to rotate almost freely in solid rare gases. In the vibrational ν_1, ν_2, and ν_3 regions, its spectrum exhibits several rovibrational lines shifted from the gas phase ones. Due to the nuclear spin of hydrogen, the rotating molecule exists in two different magnetic species (ortho- or para-magnetic). Nuclear spin conversion occurs slowly at low temperatures and is helpful to distinguish between lines associated with one or the other species. We showed recently in argon matrix that besides the absorption lines of the rotating water monomer, it remained 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 in the cage. This structure showed two maxima with conversion of the high frequency part into the low frequency one.

We will present here a study, in the mid-infrared, of H_2O in neon, argon, krypton and xenon matrices between 6 and 45 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. We will show that the RTC structure is also present in the different matrices and have different characteristics from neon to xenon. In the meanwhile, nuclear spin conversion analysis allows us to estimate the energy difference between the lowest rovibrational levels of the ortho and paramagnetic species.

BROADENING AND SHIFTING PARAMETERS FOR H_2O IN THE 3500-3650 CM^{-1} REGION

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The FTIR spectra of pure water vapor and of water vapor/nitrogen mixtures have been recorded at pressure-broadening-limited resolution in two laboratories and analyzed using a multi-spectrum non-linear least squares fitting technique[a], The measurement cells used were a heated White-type multi-reflection cell at the Kitt Peak National Solar Observatory and a heated single pass absorption cell at the Justus-Liebig-Universität Giessen. Line parameters including self- and nitrogen-broadened widths and nitrogen pressure shifts have been determined for approximately 700 main and isotopic species transitions in water vapor in natural abundance. Temperature dependence coefficients for the widths and shifts have also been determined for selected transitions in this region. Transitions for which parameters have been determined include those from the ν_1, ν_3, $2\nu_2$, $\nu_1 + \nu_2 - \nu_2$ and $\nu_2 + \nu_3 - \nu_2$ bands. Results have been compared with values available in the literature.

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THE EFFECTS OF ROTATION, VIBRATION, AND TEMPERATURE ON COLLISIONAL PARAMETERS OF H_2O LINES

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A complex semiclassical model for the calculation of line widths and shifts of H_2O broadened by N_2, derived from the Complex Robert and Bonamy (CRB) approach, is tested by comparisons with measurements for selected transitions in various vibrational bands. The lines retained, which involve rotational states with Kc=J or Kc=J-1 have been chosen for two reasons. The first is that they show large variations of the widths with J and thus enable a severe test of the model. The second is that they are well-suited for the study of the effects of rotation and vibration on the collisional parameters. The measured values have been extracted from an updated version of a database built years ago [JQSRT 1994:52;481-99] that contains all available measurements. Comparisons between experimental and calculated widths and shifts at room temperature illustrate the quality of the model and clearly demonstrate, for the first time, that there is a vibrational dependence of the broadening.
Values of collisional parameters are first studied in fundamental bands. This shows that the theoretical approach accounts for most of the dependence of broadening and shifting on rotational quantum numbers: the variations of γ, which reach a factor of nearly 20 from low to high J values, are correctly accounted for by the model as are some specific features of the shifts δ. Analysis confirms that the bending and stretching vibrations have significantly different effects on δ, due to the vibrational dependence of the intermolecular potential. On the other hand, differences on the widths are rather small with slightly smaller broadening for lines of the bending band. Calculations show that there is a spectroscopic effect, due to the larger rotational constant A in the ν_2=1 state. Calculations made for overtone bands involving numerous quanta of the stretching vibration are then presented. They predict that a significant dependence of the width should be observed for high J lines due to the effect of vibration on the interaction potential. This is confirmed by comparisons with measurements for lines involving a change of three and four quanta of stretching vibration.

ABSOLUTE LINE INTENSITIES IN THE $\nu_1+3\nu_3$ BAND OF $^{12}C_2H_2$ BY LASER PHOTOACOUSTIC SPECTROSCOPY AND FOURIER TRANSFORM SPECTROCOPY

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We carried out line intensity and self-broadening measurements in the $\nu_1+3\nu_3$ band of $^{12}C_2H_2$ near 0.8 μm by means of laser photoacoustic spectroscopy. The experimental setup mainly consisted in a cw single mode (FWHM = 500 kHz) titanium sapphire ring laser coupled with an acoustic resonant cell. Room temperature spectra were continuously recorded at pressures of 24.7 and 42.1 mbar. Laser photoacoustic spectroscopy is a highly sensitive technique, allowing to probe very weak signals. Unfortunately direct determination of absolute intensities is not possible. The spectrometer was therefore calibrated using water vapor line intensities [a] to determine absolute line intensities for the acetylene band. The validated protocol will be presented in details.
The spectrum of the $\nu_1+3\nu_3$ band was also recorded at a resolution of 0.02 cm^{-1} using a Bruker IFS120HR Fourier transform spectrometer. Spectra were recorded at room temperature and pressures of 21, 39, and 101 mbar, with an absorption pathlength of 34.5 m. The absolute line intensities measured revise previous results from the literature [b].
The photoacoustic line intensities were compared to the corresponding measurements performed using Fourier transform spectroscopy. The intensity and self-broadening measurements and the results of the comparison will be presented and discussed.
This work is supported by the EU Commission (Research Training Network No. HPRN-CT-2000-00022).

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USING FAST FOURIER TRANSFORM TO COMPUTE THE LINE SHAPE OF FREQUENCY-MODULATED SPECTRAL PROFILES

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Frequency modulation of the radiation source, coupled to phase-sensitive detection to record first and second harmonic spectra, is used in microwave and diode laser spectroscopy to improve the signal-to-noise ratio. The absorption profile recorded with detection at the nth harmonic is the nth derivative of the true line shape in the limit of low modulation frequency and small modulation depth, and is in general "modulation broadened".
In this work, an expression for the shape of spectral lines recorded by sinusoidal frequency modulation and harmonic detection is derived. It can be fast computed by means of the Fast Fourier Transform method and it holds for any modulation depth and modulation frequency. Different line shape functions, such as Voigt, Galatry and speed dependent Voigt, may be included in the model. The performance of the computing method is tested with experimental second harmonic rotational profiles, but it can be applied to higher harmonic spectra as well.

STUDY OF BROADENING AND SHIFT COEFFICIENTS OF H_2O BY H_2 AND He IN THE 1.4 μm REGION: EXPERIMENT AND CALCULATIONS

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The Groupe de Spectrométrie Moléculaire et Atmosphérique of Reims has developed a near infrared diode laser spectrometer to measure spectroscopic parameters of H_2O in the 1.39 μm region. In a previous paper[a] we have reported measurements of H_2O intensities near 1.39 μm. This work has drastically improved the accuracy of H_2O line strengths in a spectral region that is of high interest for the study of the atmosphere.

While the linestrengths and energy levels are now relatively well known, the pressure broadening halfwidths have major uncertainties that would limit water abundance determinations. For the atmospheres of giant planets such as Jupiter the broadening by H_2 and He must be known.

Hydrogen and Helium broadened halfwidths of H_2O have been measured here for 5 transitions from the $\nu_1 + \nu_3$ and $2\nu_1$ bands. We also report H_2 and He lineshift coefficients. These experimental results are compared to calculations based on semi-empirical approximation in the absorption line broadening and shift.

[a]B. PARVITTE, V. ZENINARI, I. POUCHET, G. DURRY JQSRT, **75**, pp. 493-505, (2002)

OPTIMIZATION OF FTIR SPECTROMETER FOR INTENSITY MEASUREMENTS

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The accurate determination of line intensity of individual rovibrational transition requires careful measurements on absorption path length, particle density and sample temperature. In addition, the instrumental error sources distorting for example the line shape and the proper determination of transmittance should be eliminated. In our laboratory a multireflection sample cell used in connection with a commercial high resolution Fourier transform spectrometer Bruker IFS120HR is being modified for intensity measurements.

The absorption path length of our White type cell[a] can be adjusted up to 41.6 m in steps of 3.2 m. The exact path length is determined using the interferences caused by the cell mirrors and windows. The cell is temperature stabilized and the sample temperature is measured using six Pt–100 resistance thermometers (±0.03 K) mounted into the inner walls of the cell. For stable compounds the particle density can be deduced from simple pressure measurement. The cell is equipped with a pair of MKS type 690A capacitance manometers covering the regions 0.01 – 1 Torr and 1 – 100 Torr. To maintain the absolute accuracy 0.05% the pressure transducers are calibrated yearly.

In this contribution the factors limiting the absolute accuracy in determining line intensities from FTIR spectra are discussed and some test measurements for example of the absorption path length and temperature stability will be presented.

[a] T. Ahonen, P. Karhu, and V.- M. Horneman, Contribution M4, presented at the Fifteenth Colloquium on High Resolution Molecular Spectroscopy, Glasgow, September 7-11, 1997.

CALCULATING THE QUASI-BOUND RO-VIBRATIONAL STATES OF H_3^+

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In the 1980's Carrington *et al* [a] measured a CO_2 laser predissociation spectrum of H_3^+. The spectrum had a number of remarkable features including a line density of 120 lines/cm^{-1} in the 872-1094 cm^{-1} region. As yet this spectrum remains completely unassigned.

Semi-classical analysis suggests that the spectrum consists of rotationally excited quasi-bound states (shape resonances). Our aim is to calculate the positions and widths of the rotationally excited resonance states of the molecular ion H_3^+ with a view to synthesising this spectrum. An *ab initio* potential energy surface [b] is used in conjunction with a complex absorbing potential (CAP) to model the quasi-bound states. The parallel program suite PDVR3D [c] is first used to provide accurate bound state calculations [d] in a diagonalisation, truncation, re-coupling and then final diagonalisation scheme using a discrete variable representation. The unbound state calculations are then extended using an absorbing potential to give the correct energies and widths for the resonances by diagonalising the resultant complex symmetric Hamiltonian. The resonance states are identified as stabilities in the trajectories of the Siegert energies with respect to the absorbing potential strength.

Different complex absorbing potentials were tested on HOCl (for which there are previous results [e]). It is found that the calculations are relatively insensitive to the details of the CAP but very sensitive to the convergence of the HOCl bound and unbound state calculations. In this case the majority of the error was due to basis set incompleteness.

Calculations require massively parallel computing and are being performed on the new HPCx 1280 node IBM regatta system [f] at Daresbury laboratory as part of the Chem-React high performance computing consortium. Preliminary results for H_3^+ will be reported at the conference.

1. A. Carrington I.R. McNab, *Acc. Chem. Res.* **22** (1989) 218-222
2. O.L. Polyansky, R. Prosmiti, W. Klopper, J. Tennyson *Mol. Phys.* **98** (2000) 261-273
3. H.Y. Mussa, J. Tennyson, *Comp. Phys. Comm.* **128** (2000) 434-445
4. M.A. Kostin, O.L. Polyansky, J. Tennyson, *J. Chem. Phys.* **118** (2003) 3538-2542
5. H.Y. Mussa, J. Tennyson, *Chem. Phys. Lett.* **366** (2002) 449-457
6. For further information see http://www.hpcx.ac.uk

VECTOR PARAMETRIZATION, PARTIAL ANGULAR MOMENTA AND POLYSPHERICAL COORDINATES IN MOLECULAR PHYSICS. APPLICATIONS TO INFRA-RED SPECTROSCOPY OF NON-RIGID SYSTEMS

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When studying an N-atom molecular system by means of N-1 vectors i.e. by means of a vector parametrization, one unavoidably comes across several angular momenta [a] : not only the total angular momentum of the system but also the various partial angular momenta corresponding to the motion of the various vectors, all momenta which can, in addition, be referred to a variety of reference frames [b] [c]. The use of vector parametrizations and partial angular momenta in molecular physics greatly simplifies the classical as well as quantum expressions of the kinetic energy [d]. This approach provides simple and explicit expressions of the exact and constrained kinetic energy operators which, above all, are well adapted to the numerical methods used to solve the Schrödinger equation. Several applications to the intramolecular dynamics and infra-red spectroscopy of systems such as the water dimer, H_2CO and HONO are presented [e] [f].

[a] R. N. Zare, *Angular Momentum*, Wiley, New York (1988).

[b] J. H. Van Vleck, *Rev. Mod. Phys.* **23**, 730 (1951).

[c] F. Gatti and A. Nauts, *Chem. Phys.* submitted.

[d] F. Gatti, C. Iung, M. Menou, Y. Justum, A. Nauts, and X. Chapuisat, *J. Chem. Phys.* **108**, 8804-8820 (1998).

[e] F. Gatti and C. Iung, *J. Theo. Comp. Chem.*, in press.

[f] F. Gatti, *Chem. Phys. Letters* **373**, 146 (2003).

ON THE APPLICATION OF CANONICAL PERTURBATION TO MOLECULAR DYNAMICS

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Canonical Perturbation Theory (CPT) is a powerful tool in the field of molecular physics. It consists of a series of unitary transformations, which are aimed at rewriting the Hamiltonian in a simpler form without modifying the dynamics of the problem. The goal of this poster is to report on recent results, which show how this theory can be used for investigating the highly excited dynamics of small molecules and the orientation dynamics of diatomic molecules interacting with linearly polarized laser pulses.

The first example is the molecule HCN/CNH. We have derived a modified version of CPT, which applies to floppy systems. Upon application of this procedure to a well-known ab initio surface for the HCN/CNH isomers, it has been shown that the three degrees of freedom can be considered to remain totally decoupled up to and above the isomerization barrier [a].
In the second part of the poster, we propose a new time-dependent version of CPT for studying molecular orientation driven by an electromagnetic field. The validity and the accuracy of this approach are tested on a rigid-rotor model mimicking the diatomic molecule LiCl. Using the perturbative propagator derived by this method, we also show that a non-negligible orientation can be obtained for experimentally available short laser pulses [b].

[a] M. Joyeux, D. Sugny, *Can. J. Phys.* **80**, 1459-1480 (2002).
[b] D. Sugny, A. Keller, D. Daems, O. Atabek *Phys. Rev. A*, To be submitted (2003).

MICROWAVE SPECTROMETER WITH PHASE SWITCHING FOR MOLECULAR BEAM RESEARCHES OF ORGANOMETALLIC MOLECULES

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Investigating the spectra of polyatomic organometallic molecules is of great interest in various fields of physics and chemistry. There are some difficulties caused by low intensity of their spectra as well as the presence of high intensity absorption lines of volatile impurities. For solving these problems the most effective method is the method of nonstationary mm and submm molecular beam microwave spectroscopy based on the phase switching of radiation. The microwave spectrometer based on the phase switching of radiation conjugated with vacuum set for obtaining supersonic molecular beams is presented. Spectrometer realizing this method has been fulfilled in 2-mm wavelength range. One used PLL-system for automatical control of the BWO's frequency and phase shift, time-domain registration, averaging and computer processing of the spectroscopic transient signals. Spectrometer can be operated in both scanning and Fourier transform modes. The great advantage of the phase switching spectrometer is a possibility of short time measurements, which is needed for pulsed molecular beam researches. Experimental researches of the phase-switching spectrometer demonstrate superior sensitivity, high frequency and temporal resolution, high accuracy of the spectroscopic parameter measurements and versatile application possibilities.

DOPPLER-LIMITED ROTATIONAL SPECTRUM OF THE NH RADICAL IN THE 2 THZ REGION

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The Doppler-limited spectrum of the NH radical in its electronic ($X^3\Sigma^-$) and vibrational ground state has been measured using the Cologne sideband spectrometer in the frequency region near 2 THz. The nitrogen ^{14}N nuclear hyperfine patterns have been observed accompanying the resolved fine structure of the $N = 2 \leftarrow 1$ rotational transition. The observed peak frequencies were analyzed in detail together with the previously measured hyperfine frequencies of the $N = 1 \leftarrow 0$ rotational transition (Th. Klaus, S. Takano, and G. Winnewisser, Astronom. and Astrophys. 322, L1, 1997) to derive precise rotational [$B = 489959.068(22)$, $D = 51.0344(59)$ MHz], fine [$\lambda_0 = 27577.856(19)$, $\gamma_0 = -1644.430(42)$, $\gamma_1 = 0.433(16)$, $b_F(N) = 18.829(14)$, $t(N) = -22.659(21)$, $b_F(H) = -66.120(21)$, $t(H) = 30.087(44)$] and hyperfine parameters [$eQq(N) = -3.00(14)$, $C_J(N) = 0.176(34)$] . In the numerical analysis the essential attention has been paid to the unresolved hyperfine structure. The peak positions of the partly or fully overlapped lines have been analyzed with help of a profile simulation with estimated half-widths and calculated relative intensities and by this manner the least square fit of the unresolved and partly resolved lines has been significantly improved. The NH radical is important species in nitrogen chemical reaction networks in the interstellar medium and atmospheric chemistry.

The Cologne group has been supported by the Deutsche Forschungsgemeinschaft via research grants SFB-494. We kindly acknowledge the Ministry of Science of the Land Nordrhein- Westfalen/Germany for financial support. S.U. and M.S. acknowledge support through the Grant Agency of the Czech Republic (203/01/1274). The collaborative work between the Cologne and Prague groups has been additionally supported by the International Office of the Federal Ministry of Education and Science at the DLR via grant CZE 00/030.

TOWARD THE IDENTIFICATION OF THE SUBMILLIMETER WAVE SPECTRUM OF THE BROMOMETHYL RADICAL, CH_2Br

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Bromine-containing molecules have recently received great attention because they are involved in catalytic reactions contributing in stratospheric ozone destruction. In the atmosphere, the concentration of bromomethane, the most abundant source of Br atoms, is mainly limited by its reaction with the hydroxyl radical, leading to the formation of the monobromomethyl radical, CH_2Br. This radical reacts further with other open shell species to release Br atoms for secondary reactions with ozone.

Apart from its importance in atmospheric chemistry, the study of CH_2Br is also of interest in order to compare its structure with those of its well-studied fluorine- and chlorine- analogues, CH_2F[a] and CH_2Cl[b], respectively.

In 1993, Davies et al. observed CH_2Br by far infrared laser magnetic resonance spectroscopy[c]. They generated the radical in a fast flow system by mixing CH_3Br vapour with the products of a microwave discharge in CF_4 and Ar or in F_2 and Ar mixtures. They derived approximate rotational constants. To our knowledge, no high-resolution gas-phase spectroscopic studies on this radical has been reported.

Based on their results and on recent high-level *ab initio* calculations[d], we carried out the search for the rotational transitions $N = 20 \leftarrow 19$ of CH_2Br, predicted around 446 GHz, by mixing CH_3Br vapour with the products of a 2450-MHz microwave discharge in CF_4 and Ar or in Cl_2 diluted in He. Although the recorded spectra were very congested, the comparison between both chemical reactions yielded a few common unidentified lines within the frequency range 444 - 450 GHz. All of them belong to paramagnetic species. These lines have also been detected by the 248-nm photolysis of CH_2Br_2 and by the less efficient 248-nm photolysis of CH_2BrI. The pulsed emitting mode

[a] C. Yamada and E. Hirota, *J. Mol. Spectrosc.* **116**, 101 (1986).
[b] Y. Endo, S. Saito and E. Hirota, *Can. J. Phys.* **62**, 1347 (1984).
[c] P.B. Davies, Y. Liu and Z. Liu, *Chem. Phys. Lett.* **214**, 305 (1993).
[d] J. Moc, *Chem. Phys.* **247**, 365 (1999).

of the KrF laser allowed the measurement of the lifetime of the unknown species. The measurement led to a single $1/e$ lifetime of about 50 ms for all the unidentified lines.

During this study, we have also measured new lines of CH_2Cl for both isotopic species of the Cl atoms, within the range 420 - 470 GHz. Chloromethyl radicals were generated by reaction between CH_3Cl vapour and microwave discharge in Cl_2 and He mixtures. For comparison with the lifetime of the unknown species observed by the photolysis of CH_2Br_2, we have determined the lifetime of the CH_2Cl, produced by the 248-nm photolysis of CH_2BrCl. We found that the lifetime of CH_2Cl is comparable to the one of the unknown species.

According to these preliminary results, we strongly believe that the unidentified lines belong to the monobromomethyl radical, although no assignment of the lines has been made at the time the abstract is submitted.

ROTATIONAL SPECTRUM OF BROMINATED RADICALS PRODUCED BY UV PHOTOLYSIS

P. DREAN, C. DUAN, M. HASSOUNA, A. WALTERS, M. GODON, M. BOGEY and S. BAILLEUX, *Laboratoire de Physique des Lasers, Atomes et Molécules, Centre d'Etudes et de Recherche Lasers et Application, UMR CNRS 8523, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq CEDEX, France*

Carbenes play an important role in atmospheric chemistry. Among them, brominated radicals have recently received considerable attention because they play an important part in stratospheric ozone destruction. In 2001, Sears[a] published a theoretical and experimental study of the near-infrared spectrum of the bromomethylene radical, HCBr. He obtained rotational constants and some centrifugal distortion constants for both isotopic species in the ground vibrational state. In Lille, we studied the rotational spectrum of HCBr in order to improve the constants of Sears. HCBr was produced by the 193-nm photolysis of bromoform, $CHBr_3$. Its spectrum was recorded in the frequency range 420 - 472 GHz using the kinetic detection technique. The measurement of *a*- and *b*-type transitions ensured the determination of the rotational constants as well as all the quartic and two sextic centrifugal distortion constants. The hyperfine splittings were also analysed. Nuclear quadrupole and spin-rotation coupling constants were derived for both isotopic species.

[a]H.G. Yu, T. Gonzalez-Lezana, A.J. Marr, J.T. Muckerman and T.J. Sears, *J. Chem. Phys.*, **115**, 5433 (2001)

FOURIER TRANSFORM MILLIMETER-WAVE SPECTROSCOPY OF HYDROCARBON RADICALS

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Hydrocarbon radicals are known as important reaction intermediates both in the laboratory and the interstellar space. They have also been subjected to extensive studies on molecular structure and internal motions. Microwave spectroscopy has played important roles in these studies because of its high sensitivity and high precision. However, a few important radicals such as the ethyl, vinyl, and cyclopropyl radicals, have not been studied so far with microwave spectroscopy probably because of their small permanent dipole moments. In the present study, we have undertaken to detect their rotational transitions with the Fourier transform millimeter-wave (FTMW) spectrometer, which covers the frequency range from 8 GHz to 85 GHz, in order to characterize these important radicals in detail.

The 1_{01} - 0_{00} rotational transition of the ethyl radical, C_2H_5, has been measured in the frequency region around 43.7 GHz. The observed lines show a very complicated pattern of the fine and hyperfine component lines. We have assigned the fine and hyperfine component lines with the aid of the Zeeman effect of individual lines. As a result, the most lines have been ascribed to the transitions in the ground vibrational state (A_2''). The molecular constant including the fine and hyperfine interaction constants have been determined accurately.

The 1_{01} - 0_{00} rotational transition of the C_2D_3 radical has been observed around 44.4 GHz region. The rotational constant $(B+C)/2$, the spin-rotation interaction constant, and the hyperfine interaction constants for the s and a states split by the tunneling motion associated with the C-D_α rocking mode have been determined by a least-squares analysis. The energy splitting due to the tunneling motion is discussed on the basis of the hyperfine interactions[a].

The cyclopropyl radical, C_3H_5, has so far been motivated from interest on its geometrical structure and internal motion. In the present study, we have successfully detected the 1_{10} - 1_{01} and 1_{11} - 0_{00} rotational transitions in the frequency region around 10.6 GHz and 37.4 GHz, respectively. Many fine and hyperfine component lines have been observed for each line, and their detailed analysis is now in progress.

[a]E. Kim and S. Yamamoto, *J. Chem. Phys.*, **116**, 10713-10718 (2002).

Invited Lectures N

Friday, September 12, 9:00

Chairman : M. HAVENITH

SLIT-JET IR SPECTROSCOPY: FROM MOLECULAR CLUSTERS TO HYDROCARBONS *(45 min.)*

DAVID J. NESBITT, *JILA, National Institute for Standards and Technology, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, 80309*

The combination of slit supersonic expansions and pulsed electrical discharges results in a simple yet remarkably intense source of jet cooled chemical reactive species, in a geometry ideal for shot noise limited direct absorption spectroscopy with high resolution tunable lasers. Work in our group has exploited this capability particularly in the near infrared, for which the strongly reduced Doppler linewidths (10-20 fold) in the slit jet expansion permits rovibrational, open shell fine structure and sometimes even hyperfine structure to be observed and analyzed. Most importantly, this method provides access to high resolution spectra of transient species at low rovibrational temperatures (10K), often proving crucial to the resulting spectroscopic assignment and analysis. This talk will provide a brief overview of these slit jet absorption methods, and then discuss recent progress in systems ranging from weakly bound clusters to hydrocarbon radicals and molecular ions.

NON-RIGID MOLECULES: IT IS NOW POSSIBLE TO MODEL THEIR HIGH-RESOLUTION SPECTROSCOPIC DATA *(45 min.)*

L. H. COUDERT, *Laboratoire de Photophysique Moléculaire, C.N.R.S., Université Paris-Sud, Bât. 350, 91405 Orsay Cedex, France*

It is not possible to give a comprehensive description of all non-rigid molecular systems exhibiting large amplitude motions which have been studied so far under high-resolution. However, when dealing with such systems, it is convenient to divide them into two categories depending on their number of equilibrium configurations, *i.e.*, the number of energetically equivalent minima of their potential energy surface. The first category corresponds to the case when there is only *one* equilibrium configuration, the second one to the case when there are *several* equilibrium configurations. Molecular systems belonging to this second category display large amplitude motions like, for instance, inversion or internal rotation, which lead to a tunneling splitting of their rovibrational levels. Molecular systems belonging to the first category exhibit at least one large amplitude motion, usually a large amplitude bending mode, which is strongly coupled to the overall rotation, and this leads to anomalous centrifugal distortion. Their rotational energy levels cannot be accounted for using an effective rotational Hamiltonian, like the Watson-type Hamiltonian, written as a polynomial expansion in terms of rotational angular momentum components.

The present paper will be focused on non-rigid molecular systems belonging to the second category. Progress concerning the calculation of their high-resolution spectra will be reported and various models developed to perform the calculation of their energy levels will be described. Emphasis will be made on the number of degrees of freedom considered in the model.

Poster Session O

Friday, September 12, 11:00

HIGH-ACCURACY AB INITIO ROTATION-VIBRATION TRANSITIONS FOR WATER

O. L. POLYANSKY, S. V. SHIRIN, N. F. ZOBOV, *Institute of Applied Physics RAS, Uljanov Street 46, Nizhnii Novgorod, Russia 603950*; **A.G. CSASZAR**, *Department of Theoretical Chemistry, Eotvos Lorand University, H-1518 Budapest 112, Hungary*; **P. BARLETTA,J. TENNYSON**, *Department of Physics and Astronomy, University College London, London WC1E 6BT, UK*; **D.W. SCHWENKE**, *NASA Ames Research Center, CA 94035-1000, USA*; **P.J. KNOWLES**, *School of Chemical Sciences, University of Birmingham, Birmingham B15 2TT, UK*

Absorption of light by vibration-rotation transitions of water is the single most important factor determining the structure of the atmosphere of the Earth and most cool stars. Therefore, there has long been an urgent need for a robust and accurate predictive model for this spectrum. We report first-principles calculations on the high-resolution spectrum of water that approach experimental accuracy.

The model developed here gives energy levels and hence transition frequencies for water are computed an order of magnitude more accurately than any previous ab initio study. A Born-Oppenheimer potential energy surface calculated is accurate to a few wavenumbers at 25,000 cm^{-1}. To achieve this accuracy calculations with large basis sets at the edge of modern computer capacity, are extrapolated to the full basis set limit. This sophisticated ab initio model is augmented by corrections allowing for core-valence electronic interactions and with more exotic corrections: electronic relativistic, adiabatic and quantum electrodynamics effects. Non-adiabatic corrections must also be included in the nuclear motion calculations. The high accuracy of the resulting ab initio procedure is demonstrated for the main water isotopomers[1]. Possible further improvements are identified.

Standard deviation s with which our final potential reproduces the vibrational-rotation term values for various water isotopomers with rotational excitation $\leq J_{max}$ are given in following table. N(levels) levels are considered in each case. The H_2O isotopomer calculations include rotational non-adiabatic effects.

Isotopomer	σ	J_{max}	N(levels)	Maximum Deviation	
	cm^{-1}			obs−calc	J
$H_2{}^{16}O$	1.17	20	9426	6.5	7
$H_2{}^{17}O$	0.56	12	1083	1.4	12
$H_2{}^{18}O$	0.65	12	2460	2.3	6
$D_2{}^{16}O$	0.71	12	2807	3.0	7
$HD^{16}O$	0.47	12	2019	−1.2	11
All	0.95	20	17795		

These calculations used the a 512 processor Origin3000 machine Green run by the CSAR Service at the University of Manchester; we thank the staff at CSAR for their help. We also thank the UK EPSRC, the UK NERC, the Royal Society, the British Council, the INTAS, the Scientific Research Fund of Hungary, and the Russian Fund for Fundamental Studies who supported this project.

1. O.L. Polyansky, A.G. Csaszar, S.V. Shirin, N.F. Zobov, P. Barletta, J. Tennyson, D.W. Schwenke and P.J. Knowles, *Science*, **299**, 539-542 (2003).

AB INITIO DIPOLE MOMENT SURFACE FOR THE WATER MOLECULE

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The accurate dipole moment surface (DMS) is essential for the reliable calculations of intensities of rotation- vibration transitions of water.[a] Recently a very accurate potential energy surface (PES) of water was calculated using MRCI level of theory.[b] Adiabatic and relativistic corrections to the PES proved to be necessesery to obtain the accuracy of water energy levels calculations within 1 cm^{-1}. In this work we use the above calculations to construct an accurate DMS of water. In particular extrapolation of large multireference CI calculations to the complete basis set limit is used to ensure convergence with respect to basis set expansion. The calculation of core-valence and relativistic corrections to the DMS are performed but found to be less significant. The calculations of the intensities of various water transitions using the calculated DMS and corrections will be reported at this conference.

This work has been supported by the UK Research Councils NERC and EPSRC, The Royal Society, the INTAS foundation and the Russian Fund for Fundamental Studies.

[a] A.Callegari,P.Theulé,J.S.Muenter, R.N.Tolchenov, N.F.Zobov, O.L.Polyansky, J.Tennyson, and T.R.Rizzo,*Science*, **297**, 993-995 (2002)

[b] O.L.Polyansky, A.G.Csaszar, S.V.Shirin, N.F.Zobov, P.Barletta, J.Tennyson, D.W.Schwenke, and P.J.Knowles,*Science*, **299**, 539-542 (2003)

DOPPLER-LIMITED FTIR SPECTRUM OF THE $\nu_3(a')/\nu_8(a'')$ CORIOLIS RESONANCE DYAD OF $CHC\ell F_2$ OBTAINED WITH A NEW BRUKER IFS 120HR SPECTROMETER, AND COMPARISON WITH *AB INITIO* CALCULATIONS

SIEGHARD ALBERT, HANS HOLLENSTEIN, MARTIN QUACK AND MARTIN WILLEKE, *Physical Chemistry, ETH Zurich, CH-8093 Zurich*

The Doppler-limited FTIR spectrum of this band system in the region 1070 - 1170 cm^{-1} (Doppler width $\approx$ 0.0015 cm^{-1}, FWHM) was measured with our new prototype Bruker IFS 120HR spectrometer. This instrument allows for an unapodized resolution of 0.0007 cm^{-1} (FWHM). Up to now, this is the highest resolution realized by a commercial FTIR spectrometer system. Several high resolution studies of the strongly coupled modes $\nu_3(a')$ and $\nu_8(a'')$, corresponding to the symmetric and antisymmetric CF-stretching vibrations, have been performed previously [1-3]. However, no 'complete' analysis covering the full region of these bands has been possible until now. The new Doppler-limited FTIR spectra allowed such a detailed analysis and demonstrates the high value of the improved spectral resolution.

The present analysis was based on effective rotational Hamiltonians for the $v_3 = 1$ and $v_8 = 1$ states including all terms up to quartic, and involved the full first order Coriolis interaction operator

$$\hat{H}^{3,8}_{\text{Coriolis}} = i\,\xi^{3,8}_a\,\hat{J}_a + i\,\xi^{3,8}_c\,\hat{J}_c\ .$$

The consideration of both the $\hat{J}_a$- as well as the $\hat{J}_c$- first order Coriolis terms proved essential in order to obtain a good line by line agreement between observed and calculated rovibrational structures over the full band system. In addition, the analysis of two local resonances allowed to determine the vibrational wavenumbers of the modes $3\nu_9$ and $\nu_6 + 2\nu_9$ with good accuracy. The final analysis involved the spectra of both chlorine isotopomers and included all hybrid components which are allowed by symmetry.

We also report *ab initio* calculations for this molecule on the MP2 level of theory with an aug-cc-pVDZ or a aug-cc-pVTZ basis set. Various subspaces of the potential energy and electric dipole moment hypersurface have been calculated in reduced normal coordinates including up to three dimensions. With these hypersurfaces we determined corresponding vibrational absorption spectra, comprising transition wavenumbers as well as intensities. An analysis of the vibrational levels with an effective Hamiltonian was used to derive anharmonic constants. Finally we derived Coriolis coupling constants. The *ab initio* results are compared with the present experimental findings.

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AB INITIO STUDY OF THE GROUND AND LOW-LYING ELECTRONIC STATES OF COBALT DIHALIDES, CoX_2 (X=F, Cl, Br, I)

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The ground and nine excited low-lying quartet electronic states of CoF_2, $CoCl_2$, $CoBr_2$ and CoI_2 were studied by the multiconfigurational self-consistent field (MCSCF) method. Complete active space (CASSCF) multiconfiguration calculations were carried out taking into account dynamic electron correlation at the level of second-order many-body quasi-degenerated perturbation theory (MCQDPT2). Valence triple zeta basis sets were augmented with diffuse and polarisation functions. The active space included seven electrons in six orbitals (five $3d$ and one $4s$). The cores of Br and I were described by relativistic pseudopotentials[a]. All calculations were performed by the GAMESS program package.

Equilibrium bond lengths (r_e(Co-X)), force constants, stretching vibrational frequencies (ω_1, ω_3) and relative energies (T_e) were calculated (see tables for some results). Bending potentials were investigated for the ground and six low-lying electronic states. Each potential has a minimum corresponding to the linear configuration of the molecule. This result is in agreement with the conclusion of electron diffraction investigations about the linearity of CoF_2[b], $CoCl_2$, and $CoBr_2$[c].

CoF_2:

State	T_e /cm^{-1}	r_e /Å	ω_1 /cm^{-1}	ω_3 /cm^{-1}
$^4\Delta_g$	0	1.7088	636	818
$^4\Phi_g$	1938	1.7455	614	756
$^4\Sigma_g^-$	948	1.7110	617	780

$CoCl_2$:

State	T_e /cm^{-1}	r_e /Å	ω_1 /cm^{-1}	ω_3 /cm^{-1}
$^4\Delta_g$	0	2.0522	370	539
$^4\Phi_g$	1977	2.0984	362	520
$^4\Sigma_g^-$	2959	2.0850	353	524

[a] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, and H. Preuss *Mol. Phys.* **80** (1993) 1431.

[b] N. Vogt, *J. Mol. Struct.*. **570** (2001) 189.

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$CoBr_2$:

State	T_e /cm^{-1}	r_e /Å	ω_1 /cm^{-1}	ω_3 /cm^{-1}
$^4\Delta_g$	0	2.1934	224	418
$^4\Phi_g$	1877	2.2387	222	413
$^4\Sigma_g^-$	3087	2.2327	217	413

CoI_2:

State	T_e /cm^{-1}	r_e /Å	ω_1 /cm^{-1}	ω_3 /cm^{-1}
$^4\Delta_g$	0	2.4055	159	364
$^4\Phi_g$	1556	2.4438	157	354
$^4\Sigma_g^-$	2824	2.4461	156	355

The project has been supported by the Dr. Barbara Mez-Starck Foundation.

AB INITIO ANHARMONIC FORCE FIELS AND EQUILIBRIUM STRUCTURE OF CARBONYL CHLOROFLUORIDE

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In this work, we report the calculation of a new anharmonic force field up to semi-diagonal quartic terms using a basis set of triple zeta quality. The accuracy of the force field is checked by comparing experimental and ab initio spectroscopic constants. To complete the infrared analysis reported previously [a], the present work involves also the identification of numerous overtone or combination bands of $COF^{35}Cl$, and for this task new low resolution Fourier transform spectra were recorded at Wuppertal. Finally, two independent equilibrium structures are determined: a purely ab initio one and a semi-experimental one.

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3-BUTENESELENOL : MICROWAVE SPECTRUM AND AB INITIO CALCULATIONS

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3-Buteneselenol $H_2C{=}CHCH_2CH_2SeH$ was investigated by microwave Fourier transform (5-20 GHz) and microwave Stark (24-62 GHz) spectroscopies. The spectra look rather complex due to the large number of possible conformers (15) and the number of isotopic species for selenium (6). Moreover in the Stark spectra the low-lying excited states are also detected. Quantum mechanical calculations (G2 method at the MP2 and B3LYP levels of theory) were carried to precise the relative energies of all these conformers. Their geometrical structures, centrifugal distortion constants and dipole moments were also calculated, leading to the identification of the three more stable conformers. The most stable conformer exhibits an intramolecular hydrogen bond involving the selenium atom.

AB INITIO STUDY ON THE STRUCTURE AND DYNAMICS OF PHENYLACETYLENE AND DIPHENYLACETYLENE

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The photochemical behaviors of phenylacetylene (PA) and diphenylacetylene (DPA) have been of great interest in the field of laser spectroscopy as well as material science. In spite of much effort to elucidate them, there are no reasonable pictures on the photochemistry of PA and DPA. In the present session, we report the electronic structures and dynamics of PA and DPA by means of reliable *ab initio* CASSCF and MRMP2 calculations.

As to PA, the stable structure in S_1 is optimized to be characterized as an enlarged benzene ring. The calculated rotational constants and vibrational frequencies are in good agreement with experimental findings. On the other hand, the stable structure under C_{2v} symmetry is optimized to be a quinoid structure where the aromaticity of the benzene ring is completely lost. The present S_2 optimized geometry is similar to a previous S_1 geometry by SCI calculation [a]. We will make comment on the defect of their SCI calculation. Then the internal conversion mechanism from S_2 into S_1 will be discussed, in relation with the conical intersection between S_2 and S_1. Furthermore, we will compare the photochemitry of PA with that of styrene reported recently [b, c, d].

As to DPA, the experimental findings, such as the rotational constants, vibrational frequencies, the absorption spectrum, are also well reproduced by our present calculations. The stable structure in S_0 has D_{2h} symmetry. The main transition in the low-lying excited states is A_g-B_{1u}. The most stable strcture of DPA in S_1 takes *trans*-bent form in A_u under C_{2h} symmetry. Based on reaction coordinate analysis, we will discuss how electronically excited DPA in B_1u relaxes into *trans*-bent form in A_u.

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SPECTROSCOPICALLY DETERMINED POTENTIAL ENERGY SURFACES OF WATER MOLECULE

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A potential energy surfaces for some major isotopomers of water were constructed by fitting to observed vibration-rotation energy levels of the system using the exact kinetic energy operator nuclear motion program DVR3D[a]. The starting point for the fit is the *ab initio* Born-Oppenheimer surface and corrections to it: both one- and two-electron relativistic effects, allowance for the Lamb shift and the inclusion of both adiabatic and non-adiabatic non-Born-Oppenheimer corrections[b]. Fits are made by scaling the starting potential by a morphing function, the parameters of which are optimized[c].

Two separate fits were made. In the first one the *ab initio* Born-Oppenheimer surface and corrections to it were optimized using experimental data for $H_2^{16}O$, $H_2^{17}O$ and $H_2^{18}O$ molecules together. Energy levels up to 15000 cm^{-1} with $J = 0$, 2 and 5 were fitted with only 21 parameters. Standard deviation during this fit was 0.075 cm^{-1}.

The second fit was made just for $D_2^{16}O$. Energy levels up to 8000 cm^{-1} with $J = 0$, 2 and 5 were fitted with 23 parameters. Standard deviation during this fit was 0.019 cm^{-1}. Non-adiabatic non-Born-Oppenheimer corrections are not used in the second fit.

This work was supported by The Royal Society, EPSRC, INTAS, and Russian Fund for Fundamental Studies.

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HIGH RESOLUTION SPECTROSCOPY OF BENZENE MOLECULE MEASURED BY THE COLLIMATED MOLECULAR BEAM AND ITS MAGNETIC FIELD EFFECT

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Sub-Doppler high resolution spectroscopy had been measured in 6_0^1, $6_0^1 1_0^1$ and $6_0^1 1_0^2$ vibronic bands in the $S_1\,^1B_{2u}$ electronic state of benzene. The residual Doppler width was around 30MHz and it was enough to resolve all rotational lines. The rotational structures of both $6_0^1 1_0^1$ and $6_0^1 1_0^2$ vibronic bands were revealed and the molecular constants were determined. The rotational structures of $6_0^1 1_0^1$ vibronic band was nearly regular and a perpendicular type Coriolis interaction within S_1 levels was found in the $K' = 11(-\ell')$ levels. On the other hand, the rotational structure of $6_0^1 1_0^2$ vibronic band was quite complicated. Nearly all the rotational levels below $K' < 15$ were influenced by the perturbation and exhibited short fluorescence lifetime. It indicates that the bright states interact with some dark states whose nonradiative relaxation rate constants is fast. The nonradiative rate constant of the dark states could be estimated around three times faster than that of the bright states. Zeeman spectra had also measured in magnetic field of 1.1T. The rotational quantum number dependence of the magnitude of the Zeeman broadening was nearly proportional to K among the $K = J$ levels. It indicates that the direction of the magnetic moment is perpendicular to the molecular plane. We will discuss about the origin of the magnetic moment and the dominant relaxation process of the lower vibronic bands in the $S_1\,^1B_{2u}$ electronic state.

A SUPERSONIC JET SPECTROMETER FOR TERAHERTZ APPLICATION

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The chemistry of interstellar clouds and star forming regions is quite different from terrestrial conditions. Among the molecules which have been found in the interstellar medium and in the shells of late type stars many unstable molecules like highly unsaturated hydrocarbons, light hydrids and their ions have been detected. It is most likely that many more hitherto unknown molecules will be observed in the near future, leading to a better and more detailed understanding of astrochemical processes. New astronomical instruments like the HIFI spectrometer aboard the Herschel satellite and SOFIA an airplane based telescope will open the Terahertz frequency region for high resolution observation of stellar objects and the interstellar medium.
Contrary to space where reactive species are quite abundant they are extremely difficult to be produced in sufficient amounts under laboratory conditions and thus not easy to be characterized by means of high resolution spectroscopy. It is the purpose of this newly designed spectrometer to produce unstable molecules of astrophysical relevance and to obtain spectroscopic data for their undoubted identification in space.
Backward wave oscillators (BWO) in the frequency range between 100 and 1200 GHz were used to obtain the spectra of adiabatically cooled molecules of a supersonic discharge slit source. We use a quadrupole plasma analyser to monitor and to optimise the conditions for a high yield of molecules. Technical details and first results will be presented.

OODR-STARK-SPECTROSCOPY ON JET-COOLED PENTACENE

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Rovibronic gas-phase absorption spectra of large molecules as pentacene generally exhibit only contour bands due to the extremely high density of rotational states, even in the case of rotational cooling in a supersonic jet. Using the conventional LIF-technique, unexpected large differences of the molecular polarizabilities between the the excited state A^1B_{2u} and electronic ground state X^1A_g were found by simulating the complete but unresolved Stark-spectrum of the band contour.

The advantages of the optical-optical double resonance (OODR)-technique have been shown recently to determine precise rotational constants by detecting individual rovibronic transitions[a]. In our report we demonstrate the possibility to measure electric field shifts of single rovibronic lines in congested spectra by using the OODR-technique. About 40 single OODR-lines in the vibrationless $S_1 \leftarrow S_0$ transition of pentacene were observed at field strengths up to 25 kV/cm. The large value of $\Delta\bar{P} = 6100$ *a.u.*[b] was confirmed and the polarizability differences can be determined without ambiguity. The results are explained qualitatively by a dominating contribution of vibrational polarizability due to low frequency (floppy) vibrational modes.

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HIGH SENSITIVITY NEAR INFRARED SPECTROSCOPY OF PEROXY RADICALS IN SLIT SUPERSONIC EXPANSION

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Spectroscopic detection of many un-bottable species such as radicals and ions has been elusive for long time due to low attainable concentrations of such species, resulting in absorption signals that are several orders of magnitude weaker than those typical for stable molecules. Combination of new techniques for production of high densities of the species of interest with high sensitivity detection is therefore needed in such cases. In our experiment, described in detail in this contribution, we use high sensitivity cavity ring down detection technique in combination with slit nozzle radical source to study the the low-lying electronic transitions in the near IR spectral region. Specifically, the radicals are produced in electric discharge confined at the throat of a slit supersonic nozzle (4cm long, 0.2mm wide) and are efficiently cooled in the subsequent supersonic expansion. This leads to reduction of Doppler widths of the observed spectral lines and overall spectra simplification. High resolution near IR diode laser spectrometer with high sensitivity cw cavity ring down detection is used to measure the absolute absorption coefficients. We also present a preliminary results from near IR absorption spectroscopic study of organic peroxy radicals (ROO, R=CH3, C2H5) near 1380nm .

HIGH-RESOLUTION SPECTROSCOPY OF THE $S_1 - S_0$ TRANSITION OF NAPHTHALENE IN A COLLIMATED MOLECULAR BEAM

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The main dynamical process in the lower vibrational levels of the S_1 $^1B_{1u}$ state of naphthalene is intersystem crossing to the triplet state. By Doppler-free high-resolution two-photon absorption spectroscopy, it has been shown that the magnetic moment in the 21^1 level arises from the interaction with the $^3\sigma\pi^*$ state and the direction is perpendicular to the molecular plane . [a] Using the collimated molecular beam technique, we have observed high-resolution spectra and Zeeman splitting of each rotational line for the 33_0^1 band. [b] In the present study we made the same measurements for other prominent vibrational bands. The observed linewidth was 0.0007 cm^{-1} and the absolute transition wavenumber was calibrated with the accuracy of 0.0002 cm^{-1} using Doppler-free high-resolution spectral atlas of iodine molecule. [c] The accurate molecular constants and the magnetic moments have been determined for each vibrational level. The amplitude of the magnetic moment was found to be remarkably different with the vibrational and rotational levels. We present the results of the high-resolution spectroscopy and discuss the dependence of singlet-triplet coupling and intersystem crossing rate on the vibrational and rotational levels in the S_1 $^1B_{1u}$ state of the isolated naphthalene molecule.

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FOURIER TRANSFORM FREE-JET SET-UP FOR THE SPECTROSCOPIC INVESTIGATION OF VERY HOT GASES

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A number of astrophysical objects, ranging from giant planets to brown dwarves, are characterised by moderate surface temperatures (up to 3000 K). The near infrared absorption spectra of such objects is used to determine several parameters (as surface temperature, chemical composition, photosphere pressure) of crucial importance for their modelling. The accuracy of the extracted parameters relies upon the validity of the model used to reproduce the infrared spectra of the observed molecules. Infrared spectral lines of the various observed molecular species (such as methane [a]) are required at temperatures up to 3000 K in order to improve their infrared signature modelling.
We have developed a continuous supersonic nozzle whose reservoir can be heated up to 1500 K. The free expansion can be probed before or after the normal shock wave (Mach disk). The first zone, characterised by high vibrational but low rotational temperatures, is well suited for counting the hot bands and then determining the highly excited vibrational states. In the second zone, hot temperature spectroscopy can be carried out in thermal equilibrium conditions at the temperature of the reservoir.

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INVESTIGATION OF THE VIBRATIONAL ENERGY PATTERN IN THE DIMER OF FORMIC ACID

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We recorded spectra of the dimer of formic acid under various experimental conditions, using FTIR. Higher pressure conditions allowed room temperature data to be recorded in the mid and far infrared regions, with single and multiple pass absorption cells. Jet-cooled data were also recorded in the infrared region. Some very partly resolved structure is observed in both the far infrared and jet cooled data. Simulation of the rotational band contour allows the rotational temperature in the jet to be estimated to about 35 K.
The poster will report on the various observed band heads and their assignment.

THE NO DIMER : ARE THE LIFETIMES OF THE ROVIBRATIONAL LEVELS, IN THE $V_5 = 1$ STATE, ROTATIONALLY DEPENDENT ?

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The ν_5 fundamental transition of the NO dimer has been revisited [1] by high resolution Fourier Transform Infrared spectroscopy. The NO dimer was produced in the continuous expansion of a low-pressure argon seeded supersonic jet. The dimer formation was enhanced by monitoring both the temperature (170 K) and the total pressure (500 mbar), upstream from the circular nozzle. The dimer absorption was magnified by using a multipass White-type optical set-up which allowed the IR beam to cross 16 times the molecular jet. Finally, the statistical noise in the jet-FTIR spectrum was reduced by coadding more than 2600 scans at 0.05 cm^{-1} resolution. The experimental absorption profile of the ν_5 band was then compared with several calculated rovibrational contours. The rotational temperature and the homogeneous linewidths, directly related to the lifetimes of the excited rovibrational states, were varied. Three series of calculations were performed : (i) with a J'-independent lifetime, (ii) with J'-dependent lifetimes, (iii) with J'- and K'_a-dependent lifetimes (J' and K'_a being the rotational numbers of the upper states of the transitions). The evidence for a rotational dependence of the lifetimes of the rovibrational levels in the $V_5 = 1$ excited state of $(NO)_2$ will be discussed from comparison between experimental and calculated profiles.

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POLARISATION LABELLING SPECTROSCOPY TECHNIQUE APPLIED TO HETERONUCLEAR ALKALI DIMERS: RECENT RESULTS FOR KLi, NaK AND NaRb

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For a number of years we have been involved in investigation of alkali dimers, studying excited electronic states accessible in one photon transitions from the ground states. We have been using the polarisation labelling spectroscopy method[a]. This technique elegantly surmounts the difficulty of resolving and analyzing highly congested molecular spectra. With a proper choice of frequencies and polarisation of two laser beams, interacting with a given molecular sample, only transitions from a few known rovibrational levels in the ground state are observed, resulting in spectra with easily resolved and understandable rotational structure.

Our variant of the method is based on the V-type optical-optical double resonance excitation scheme employing two independent laser sources[b]. The probe laser has a fixed frequency and excites a few assigned transitions in the investigated molecule. The pump laser is either a dye laser or the optical parametric generator (coupled with a frequency doubler) and in both cases the pump light is tuned over a broad spectral range of interest. The polarisation spectra are Doppler-limited but they are greatly simplified in comparison to classical absorption spectra due to the labelling process. The precision in determination of molecular constants from such experiments is adequate to chemical needs and fully sufficient for comparison with modern ab initio calculations.

One of the subjects of our experiments were heteronuclear alkali dimers, which are the prototypes of diatomic, heteronuclear systems for which both spectroscopic measurements and quantum mechanical calculations are feasible. In the past years we have characterised[c] 6 electronic states in NaK, $4^1\Sigma^+$ to $6^1\Sigma^+$ and $3^1\Pi$ to $5^1\Pi$ and 4 states in KLi, $X^1\Sigma^+$, $B^1\Pi$, $C^1\Sigma^+$, and $D^1\Pi$.

In this contribution we present the first experimental observation of:

- the $6^1\Pi$ and $7^1\Pi$ state in NaK, correlating with the atomic states Na(3S) + K(4F) and Na(3S) + K(6P), respectively;

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[b] W. Jastrzebski and P. Kowalczyk, *Phys. Rev. A* **51**, 1046 (1995).

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- the $4^1\Pi$ state in KLi, dissociating to K(5P)+Li(2S) atoms;
- the $4^1\Pi$ state in NaRb, corresponding to the atomic configuration Na(3S) + Rb(6P).

The examples of the spectra and details of their analysis will be shown together with potential energy curves of the investigated states, deduced from the experimental observations. The obtained interatomic potentials will be compared with the existing theoretical ones.

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PECULIARITIES OF ATOM-DIATOM COLLISION COMPLEX FORMATION: CLASSICAL TRAJECTORY STUDY

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Tightly bound bimolecular complexes in the gas phase are formed usually in the course of a third-body stabilization of their precursors–quasibound complexes (collision complexes, or Feshbach resonances). The latter can form provided at least one of the colliding partners has an internal degree of freedom. In the present paper the peculiarities of the quasibound complexes formation in collisions of an atom with a rigid quasi-diatomic molecule are studied making use the method of classical trajectories. Carbon dioxide–Ar system is taken as an example. Statistical distributions characterizing the formation of collision complexes and those appropriate to rotational relaxation cross sections are simulated and analyzed. The cross sections and thermal rates for complexes formation are obtained using Sorbie-Murrell model. The following factors are examined in what concerns their role in the formation of the quasibound complex: 1) the depth of complexity of a trajectory approach (exact classical, planar, coplanar); 2) the type of the selected intermolecular potential (*ab initio*, Lennard-Jones, etc.); 3) the departure of the initial rotational or translational distributions from the equilibrium.

THE STUDY OF THE WATER–CARBON DIOXIDE COMPLEXES: FTIR SPECTROSCOPY IN VARIOUS MATRICES AND ANHARMONIC VARIATIONAL CALCULATIONS

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The interaction between water and carbon dioxide is long recognized to be of vital importance in nature. Both parent species are ubiquitous either in biological environments, in atmosphere, or in space. In spite of extensive efforts to characterize H_2O–CO_2 weakly interacting system, many important details are still barely understood. New in-depth researches are thus worth of doing.

The T–shaped equilibrium structure of an isolated H_2O–CO_2 vdW complex was established in a pioneering work by Peterson and Klemperer[a] in a molecular beam. This geometry is fully consistent with subsequent low-temperature observations either in the jets or in the matrices, as well as with extensive *ab initio* examinations of the potential energy surface. There are some indications, however, that a hydrogen bond can form between water and carbon dioxide molecules.[b]

Present study pursues two principal goals. First, the results of new FTIR observations of H_2O–CO_2 complexes trapped in various matrices are reported either in the range of CO_2 (in Ne Ar, N_2, and Kr matrices) or in the range of H_2O (in Ar and N_2) vibrations. This made it possible to significantly enlarge the available set of data on the vibrational frequencies and transition intensities for these trapped vdW species. No signatures of the H-bonded isomer were found in the matrices. Second, extensive anharmonic variational calculations were made for both vdW and hydrogen bonded isomers starting from 6-31G(2d,2p)/MP2 *ab initio* trial approximation. This allowed for a solution of inverse spectroscopic problem resulting in evaluation of the parameters characterizing the potential energy and the dipole moment surfaces for the

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interaction between H_2O and CO_2.[c]

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A SIMPLE ANALYTICAL PARAMETERIZATION FOR THE WATER VAPOR MILLIMETER WAVE FOREIGN CONTINUUM

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We present a theoretical calculation of the millimeter wave foreign continuum due to colliding pairs of $H_2O - N_2$ molecules. It is based on the Lanczos algorithm, and the resulting tri-diagonal matrix is written in terms of continued fractions. The calculations are carried out in the coordinate representation in which the basis functions are delta functions whose arguments are the angular variables necessary to specify the molecular orientations. In this representation, the anisotropic interaction potential responsible for the continuum absorption is diagonal, and the ensemble averages over the states become multidimensional integrations. These are computed using the Monte Carlo method. The results, computed for a range of temperatures relevant to the atmosphere, are compared to laboratory measurements and to widely used empirical models. For easy use, we fit our results for the absorption coefficient (in dB/km) to a simple analytic function of frequency f applicable up to 450 GHz and temperature T ranging from 220 K to 330 K: $\alpha(f,T) = 1.918 \times 10^{-7} P_{H_2O} P_{N_2} (300/T)^{4.587} f^{2.045}$, where P_{H_2O} and P_{N_2} are given in kPa.

ABSORPTION CROSS-SECTIONS OF FORMALDEHYDE BY FOURIER TRANSFORM SPECTROMETRY: UV-VISIBLE AND IR INTERCOMPARISON

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This work is part of a series of experiments devoted to the intercomparison of the IR and UV-visible absorpion cross-sections of molecules by Fourier transform spectrometry. The experimental setup is made so as the UV-visible and IR beam go through the gas in the same path and in the same time.Two Bruker Fourier transform spectrometers (one from the U.L.B. and one from the I.A.S.B.) were used simultanously with the multipass cell at Reims University, to register both regions. In the frame of that experiment, we measured room temperature formaldehyde cross-sections in the regions 2840-3180 cm^{-1} in the IR (resolution: 0.005 cm^{-1}) and 28000-39000 cm^{-1} in the UV-visible (resolution: 1 cm^{-1}). The IR spectra contain additional large absoption bands that we identified as being due to the presence of gas phase trioxane (the cyclic trimer of formaldehyde) in the absorption cell. Using IR spectra recorded at different pressures, we were abled to determine partial pressures of each compound and then the UV-visible absorption cross sections of formaldehyde. Results will be presented and discussed

WEAKLY-BONDED COMPLEXES: HOW TO INTRODUCE SIMULTANEOUSLY QUANTUM INDIRECT DAMPING AND DAVYDOV COUPLING

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In order to explain infrared lineshapes of the ν_{X-H} stretching mode of hydrogen-bonded complexes[a], a new approach of the combined effects of quantum indirect damping and of Davydov coupling is proposed[b]. As in an older model[c], the indirect relaxation of the H-bond bridge is described using the driven damped quantum harmonic oscillator model[d]. The corresponding Hamiltonian operator is obtained in a non-hermitean reduced form[e]. This Hamiltonian is then introduced in the Davydov coupling model of Maréchal and Witkowski[f], and the IR lineshape of the ν_{X-H} stretching mode obtained within the linear response theory. Some numerical experiments, performed for different values of the indirect damping parameter and of the Davydov coupling, allow us to stress their main effects on the infrared lineshapes.

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VIBRATION AND ROTATION *S*-VECTORS, AND ROVIBRATIONAL HAMILTONIAN FOR FIVE ATOMIC MOLECULES OF A TYPE $XONY_2$

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As it is well-known, the knowledge of Wilson's vibration s-vectors and their rotation counterparts together with the Jacobian of the transformation from the Cartesian coordinates to internal ones gives the full information about the rovibrational Hamiltonian of a molecule. The s-vectors are known for valence coordinates, however they are inconvenient for molecules executing the inversion motion.

Here, we present new s-vectors based on the coordinates adapted for describing of the large-amplitude molecular motions including the torsion and the inversion motions in five atomic molecules of type $XONY_2$. The overall molecular rotation and the internal motions of the ONY_2 molecule subgroup are defined by umbrella-like coordinates [1]. The ONY_2 subgroup forms the molecular rotating frame spanned by its three valence vectors with the origin in the central nucleus N. The molecular z-axis is parallel to the trisector of the pyramidal angle formed by the three bond vectors. This angle determines the inversion coordinate. The motion of the peripheral nucleus X relative to the ONY_2 frame is described by the standard valence coordinates. These are the bond length r (OX), the bending angle β (XON), and the dihedral angle ϕ between the plane XON and the plane which goes through the bond ON and the z molecular axis. These coordinates play the role of the polar-spherical coordinates for this nucleus with the well-known Jacobian [2]. The Jacobian for the subgroup ONY_2 was derived earlier by us [1] and independently by Handy et al [3]. The full Jacobian is the product of these two known parts. One of them refers to the valence coordinates and the second one to the umbrella-like coordinates.

The derived vibration and rotation s-vectors for the specified internal coordinates and rotating axes are expressed through valence vectors and basic orts of the molecular system of axes. They take a simple form and reflect the symmetry of the molecule. The construction of the rovibrational Hamiltonian is reduced to a straightforward determination of dot products of the specified s-vectors under known formulas. These products are easily carried out by hand without use of any mathematical packages. In the report all elements

of the vibration, Coriolis, and rotation matrix of kinematic coefficients of the Hamiltonian are presented.

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"EXACT" AND "PLANARITY-CONSTRAINED" KINETIC ENERGY OPERATOR FOR A MOLECULE OF MALONALDEHYDE

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Malonaldehyde and related molecules are used as important prototypes for the theoretical and experimental investigation of proton tunneling in polyatomic systems. A straightforward calculation of the tunneling splitting in these molecules requires of knowing of the many-dimensional potential surface. Now such surfaces are intensively determined. But since they are strongly anharmonic and complicated, direct methods would not do, and such a calculation would be beyond our possibilities.

For such large systems, model constraints must be introduced to simplify the problem. In this case, there is no need for any potential data concerning the corresponding frozen degrees of freedom. However, the corresponding exact Hamiltonian cannot be straightforwardly written, even if the kinetic energy operator for the constraint free system is known. Indeed, imposing model constraints modify the metrics of the configuration space, so differential operators must also change.

"Exact" and "planarity-constrained" kinetic energy operators are proposed for Malonaldehyde. Constructing of these operators is based on a separation of the molecule into two subsystems: the first one consists of the $O-H-O$ fragment and the second one comprises the remaining molecular atoms. Molecular dynamical variables are expressed in terms of spherical coordinates of the valence vectors and the Jacobi vector, which passes from the center of mass of the first subsystem to the center of mass of the second subsystem. The actual construction is firstly performed for the "exact" operator (for more details see Ref.[1]). Further, we pass to a planar configuration of the molecule freezing azimuthal angles of the vectors. Here we follow to the method of the work [2]. Derived the "planarity-constrained" Hamiltonian has enough simple form analogous that for the free system. A contribution of the constraints is transmitted in an extra potential term, which can be easily calculated numerically. Under the chosen set of the vectors Coriolis interaction in the Hamiltonians is very small.

The resulting kinetic energy operators form a very general basis for studying the dynamical dimensionality of the proton transfer motion within the $O - H - O$ intramolecular hydrogen bond of the studied systems (see, e.g., Ref. [3]). Due to relatively small magnitudes of their Coriolis terms, the operators appear also suitable for ro-vibrational analyses.

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A THEORETICAL STUDY OF THE ROVIBRATIONAL ENERGY LEVEL STRUCTURE IN THE GROUND ELECTRONIC STATE OF DIAZOCARBENE [CNN]

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For the first time a completely theoretical investigation of the rovibrational energy level structure in the ground electronic state $\tilde{X}^3\Sigma^-$ of CNN radical is carried out. The potential energy surface of the state was calculated employing the MRD-CI *ab initio* method [a] with an aug-cc-pVTZ basis set [b]. Fitted force constants were used for MORBID [c] calculations to create a synthetic rotation-vibration spectrum. The obtained molecular and spectroscopic constants are found to be in a good agreement with existing experimental results and previous *ab initio* studies.

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INVESTIGATION OF IMPURITIES OF TETRAFLUOROSILANE BY MICROWAVE GAS SPECTROSCOPY METHOD

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The present paper deals with possibilities of using of microwave gas spectroscopy method advantages of which are the high resolution and the unambiguous determination of investigated substances by measurements of absorption spectra. The presence of molecules of freons such as fluoromethane, difluoromethane, trifluoromethane in impurity composition of tetrafluorosilane was expected. The absorption lines characteristics of these molecules are considered here theoretically. The frequencies and absorption coefficients of rotational transitions are estimated by using of known rotational constants and dipole moments. The known absorption lines of these molecules are also used for identification of experimental spectrum. The experimental measurements of microwave spectrum of system tetrafluorosilane-impurities were taken with phase-switching microwave spectrometer in 115-183 GHz frequency range. The absorption lines of molecules fluoromethane, difluoromethane, trifluoromethane were detected. The characteristics of absorption lines are in good accordance with results of theoretical analysis.

MICROWAVE SPECTRUM AND INTRAMOLECULAR HYDROGEN BONDING IN 2-BICYCLOPROPYLIDENYLMETHANOL

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The microwave spectrum of the title compound has been investigated in the 26-62 GHz spectral range. Nine different conformers are possible for this compound, three of which are stabilized by intramolecular hydrogen bonds. One of these three rotamers has been assigned. This rotamer has an internal H bond and is predicted by ab intio calculations (MP2/6-311++G** level) to be the most stable form of the molecule. The microwave spectrum is weak and it is quite likely that further rotamers co-exists with the one assigned here in rather large proportions.

MICROWAVE SPECTRUM AND STRUCTURE OF 1-THIA-*CLOSO*-DODECABORANE(11), 1-$SB_{11}H_{11}$

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1-Thia-*closo*-dodecaborane(11), 1-$SB_{11}H_{11}$ is a rather rare example of a symmetrical top having C_{5V} symmetry. The microwave spectra of several isotopomers have been assigned and an accurate substitution structure of the heavy-atom skeleton has been determined. It was found that the sulfur atom leads to substantial elongation of the distances between the boron atoms in the ring closest to the sulfur atom, as compared to the distances in the remote ring. The MW structure is in good agreement with a previous electron-diffraction investigation, and with B3LYP/cc-pVTZ calculations.

UV-LASERSPECTROSCOPY ON 9-(CYANO)-ANTHRACENE

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An investigation of the rotational structure of the vibrationless $S_0 \rightarrow S_1$ transition of 9-cyano-anthracene at 382 nm is presented. The rotational constants of the electronic ground and first excited state were determined and good agreements were found with results of quantum chemical calculations.

UV-LASERSPECTROSCOPY ON 9-(N-CARBAZOLYL)-ANTHRACENE IN ELECTRIC FIELDS

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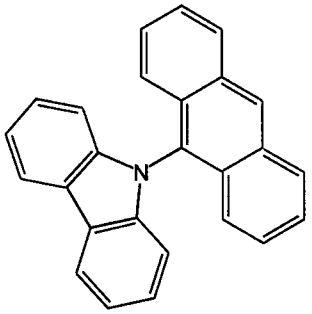
The molecule 9-(N-carbazolyl)-anthracene (C9A) depicted to the right has been shown to exhibit a resonant dark reaction in molecular beam experiments (2,3). Investigations in solution revealed the possibility of the formation of a photoinduced intramolecular charge transfer state similar to 9,9'-bianthryl (1). Recent theoretical investigations supported the attribution of the dark-reaction in the molecular beam experiments to a reaction populating a charge transfer state (3). Furthermore the mode-selectivity of the reaction could be identified for the molecule by means of cavity ring-down spectroscopy.



C9A

Now we focus on high resolution cw-laser spectroscopy in an electric field. By evaluating the Stark-effect, information about the molecular electric properties especially the dipole moment could be derived. The idea is to determine the dipole moment at different excitation energies. Finding a higher dipole moment in the excitation range of the resonant dark reaction would be a clear indication for the charge transfer character of the dark state.
The Stark-effect measurements of different torsional lines of the $S_0 \rightarrow S_1$ transition — within the energetic excitation range of the resonant reaction and below — are presented.

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VACUUM-ULTRAVIOLET (10–27 eV) PHOTODISSOCIATION OF ETHYLENE ($H_2C=CH_2$) AND ALLENE ($H_2C=C=CH_2$) STUDIED BY FRAGMENT DISPERSED FLUORESCENCE

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These molecules as well as their neutral photodissociation products play a crucial role in the carbon chemistry of several astrophysical media such as planetary and cometary atmospheres or circumstellar envelopes of carbonated stars. C_2H_4 and C_3H_4 are suspected to be C_2 and C_3 photolysis parents in the atmospheres of the carbon star IRC+10216 and of comets. The various photodissociation mechanisms are not yet well understood.

In the present work the photoabsorption and fluorescence excitation spectra of ethylene and allene have been recorded using monochromated synchrotron radiation in the excitation wavelength range 110–50 nm. Dispersed visible fluorescence of the photofragments CH, C_2, C_2H and H has also been recorded between 400 and 900 nm. Different apparition thresholds are measured and corresponding fragmentation pathways are identified. Experimental evidence for the role of the ethylidene (H_3CCH) and the propyne (H_3CCCH) isomers in this VUV photolysis of ethylene and allene respectively are presented.

THRESHOLD AND HIGH-FREQUENCY PECULIARITIES IN DIPOLE-BOUND ANION PHOTODETACHMENT

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Considerable attention is payed presently to so-called dipole-bound anions (DBA), *i. e.* molecular negative ions in those the excess electron is bound to the molecular neutral due to its dipole moment (see, for instance, [1] and references therein). Such structures play important role in various physical, chemical and biological processes.

We use simple model which considers DBA as an electron moving in a point dipole potential. The developed simple analytic theory allows to explain some features of frequency-dependent DBA photodetachment. While the most of experimental photoelectron spectra [1] are recorded at a constant photon frequency ω, the Reference [2] reports the photodetachment rate $\propto \omega^{-2}$. Such a behaviour is distinct of the photodetachment cross-section $\propto \omega^{-3/2}$ in atomic negative ions, and can be easily predicted using the proposed analytical technique. Our approach also predicts the Gailitis-Damburg oscillatory behaviour of the cross-section near the threshold.

The problem was considered both in Born-Oppenheimer and inverse Born-Oppenheimer approximations. The photodetachment cross-section is expressed in terms of hypergeometric functions and in limiting cases it is determined by

$$\sigma \propto \begin{cases} \omega^{-2}, & \hbar\omega \gg |E| \\ \cos^2\left[a \ln(k/\varkappa) + b\right], & k \to 0, \end{cases}$$

where $E = \hbar^2\varkappa^2/(2m)$ is the electronic affinity of DBA, k is the electron wavenumber in final state, the a and b constants are dependent on the DBA dipole moment.

Acknowledgements

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INDUCED DIPOLE EFFECT ON PHOTODETACHMENT OF NEGATIVE IONS

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The effect of a field-induced dipole moment of the ionic core on the transition probability of the optical electron (the Bersuker–Veselov correction) is a well-known fact [1,2]. An analogous effect in the bremsstrahlung process is also well studied, both theoretically and experimentally [3]. In this report we analyze the role of the dipole moment induced in the neutral atom in the process of photodetachment of a corresponding negative ion in a strong laser field.

The recent experiment on negative ion photodetachment [4] demonstrates a good agreement with the Gribakin–Kuchiev (GK) adiabatic theory of multiphoton detachment [5], which reexamines and extends the famous Keldysh theory [6]. Our calculations are based on the GK theory modified to take into account the induced dipole moment.

The external linearly polarised a.c. field of strength F and frequency ω induces the dipole moment

$$d = \alpha(\omega) F \cos \omega t \quad , \tag{1}$$

where $\alpha(\omega)$ is the dynamic polarizability of the atom. A consequence of the induced dipole is the non-spheric symmetry of the potential in which the outer electron moves. The non-sphericity can be accounted for on a basis of the exact solution of the Schrödinger equation for an electron moving in the Coulomb + point dipole potential. This model was proposed before for the description of Rydberg electrons in polar molecules [7,8]. The main effect of this non-sphericity is expressed in terms of modification of the angular distribution of photoelectrons. The induced dipole also modifies the pre-exponential field dependency of the photodetachment probability.

A simple preliminary estimation shows that for $\alpha \sim 100$ a.u. and $F \sim 0.001$ a.u. the induced dipole effect on the integral photodetachment cross-section is approximately 10%.

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FLUORESCENCE LIFETIMES OF THE $\overline{H}\ ^1\Sigma_g^+$ AND R $^1\Pi_g$ STATES OF D_2

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The vibronic structures of excited gerade manifolds of molecular hydrogen and its isotopomers have been the subject of extensive experimental and theoretical research. The recent progress of wavelength up-conversion technique involving four-wave mixing enabled us to populate single rovibronic levels of gerade states via B $^1\Sigma_u^+$ as an intermediate state. The fluorescence lifetimes of the EF, GK $^1\Sigma_g^+$, I $^1\Pi_g$ and J $^1\Delta_g$ states have been measured by our group since 1992. The rotational level dependence of observed lifetimes is well interpreted by the nonadiabatic couplings among upper manifolds. In the current experiment, we measured the fluorescence lifetimes of the $\overline{H}\ ^1\Sigma_g^+$ and R $^1\Pi_g$ states of D_2 which are located above the second dissociation limit (D 1s + D 2s, 2p).

$\overline{H}\ ^1\Sigma_g^+$: The fourth $^1\Sigma_g^+$ state with a double minimum potential is called H$\overline{H}$. The outer well part is denoted as $\overline{H}$. Its broad potential minimum is located at an internuclear separation as large as 6 A and at an energy of about 15 eV above the ground state. The v = 0 level is just 0.22 eV below the ionization threshold. Rovibronic structures of the $\overline{H}\ ^1\Sigma_g^+$ state of H_2 and D_2 have been investigated by Ubachs and co-workers [1]. They also evaluated the lifetimes by a pump-and-probe method with an ion detection. In the present study, we succeeded in obtaining more accurate values by measuring the fluorescence decay directly. The overall agreement between our and their values is fairly good. Several new findings are as follows:

1. Lifetimes are independent on rotational levels within the same vibrational quantum number between v = 9 and 17. They become longer from 56.7 ns (v = 17) up to 77.6 ns (v = 9).
2. The lifetimes for v = 18 vary from 8.0 ns (J = 2) up to 50.9 ns (J = 4). The lifetimes for v = 19 are even shorter than those of v = 18.

R $^1\Pi_g$: Term values of the R $^1\Pi_g^-$ (v = 0 - 6) states of D_2 have been known from the emission studies [2]: only the v = 0 level is located below the second dissociation limit, whereas the ionization threshold is between v = 4 and 5. In the present study, the R $^1\Pi_g^-$ state is populated through the double resonant excitation via the C $^1\Pi_u$ state. The fluorescence lifetimes have been measured for v = 4 - 7, J = 1 - 4.

1. The $^1\Pi_g^+$ component was not detectable.
2. Lifetimes for v = 4 - 6, J = 1 - 4, ranging from 38 to 52 ns, exhibit only a slight rotational dependence except for v = 5, J = 3 and v = 5, J = 4 where much shorter decays of 18 ns and 8.6 ns are observed, respectively.

3. A sudden reduction of the lifetimes (below 10 ns) occurs at v = 7, suggesting the existence of nonradiative decay channel(s).

[1] E. Reinhold, W. Hogervorst, and W. Ubachs, J. Chem. Phys. 112, 10754(2000).
[2] R.S. Freund, J.A. Schiavone, and H.M. Crosswhite, J. Phys. Chem. Ref. Data 14, 235(1985).

SIMULATION OF HOT CARBON DIOXIDE SPECTRA

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The caracteristics of high-temperature spectra of carbon dioxide are often needed for the solution of various applied problems of the atmospheric spectroscopy. In some cases the information on the caracteristics of spectra radiation at very high temperatures, up to the temperature of molecule dissociation, is indispensable. In this report we present an approach that has been developed for calculation of various spectral characteristics of CO_2.

The calculations use a database of CO_2 spectral line parameters [a]. This database contains parameters (positions, intensities, self-broadened halfwidths, quantum numbers) of 49101750 lines of isotopomer $12C16O_2$ in the range 700 – 10730 cm^{-1} at the temperature 4000 K. Depending on the spectral area, the intensity cutoff threshold of a line varies from 10^{-27} to 10^{-30} cm^{-1} / (molecule$*cm^{-2}$). This approach faciliates the calculations of various characteristics of emissivity and transmittance spectra in spectral intervals of any width at temperatures higher than 600 – 800 K.

Comparison of the spectral characteristics calculated by this approach with published results of an experimental research has shown their good conformity. It is revealed, in particular, that at temperatures 1300 – 1500 K the correspondence of our calculations with the latest experimental measurements [b] is much better compared to the calculations executed on the basis of the database HITEMP [c].

1 V.M. Osipov. The database for calculations of CO_2 spectral characteristics by high temperatures, Abstracts of International Symposium "Atmospheric Radiation", St.-Petersburg State University, 85 (2002).

2 M.F. Modest, S.P. Bharadway, *J. Quant. Spectrosc. Radiat. Transfer*, **73** 329-338 (2002).

3 L.S. Rothman et al. HITEMP, the high-temperature molecular spectroscopic database, is being prepared for the JQSRT, The HITRAN web-site, http://CfA-www.Harward.edu/HITRAN.

EMISSION SPECTRUM OF HOT D_2O IN 380–1800 CM^{-1}

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The hot (T=1800 K) spectrum of D_2O was recorded in 1997 at the University of Waterloo with a Bruker IFS 120 HR Fourier transform spectrometer with resolution 0.01 cm^{-1} at 2.5 Torr pressure. The lines were measured with the WSpectra program of M. Carleer and have an estimated accuracy of 0.001 cm^{-1} for strong unblended lines. The spectrum was very dense with H_2O, HDO, and D_2O lines present.

We report here an analysis of the low frequency part of the spectrum in 380-1880 cm^{-1} region occupied mostly by pure rotational and fundamental and hot ν_2 bands transitions. The first step in analysis is to identify those lines belonging to D_2O emission. In experimental linelist, containing about 16 000 lines, 2095 lines could be identified as belonging to HDO and a further 820 lines as belonging to H_2O by comparison with published hot emission spectra of HDO and H_2O. For the further analysis semiemperical linelist of D_2O transitions with J up to 30 was constructed. The next step was 'trivial' assignment using known D_2O rotation-vibration energy levels and the theoretical linelist. This resulted in 2960 transitions.

Having eliminated trivial assignments and other isotopomers from our list of transitions, the unassigned lines were analyzed using a computer program. Candidate transitions were identified using the variational linelist and then confrmed, or discarded, by the presence or lack of the appropriate combination difference transitions. Quite a lot of transitions involving levels with high J and K_a values were assigned by direct comparison with theoretical predictions as there was only one strong pure rotational transition with the level. In this way we were able to identify 3240 new transitions leading to determination of about 2000 new energy levels in vibrational states (000), (010), (020), (030), for which low-lying energy levels are already known, and for the first time to the (040) and (050) vibrational states.

This work was supported by The Royal Society, INTAS, EPSRC and Russian Fund for Fundamental Studies.

TEMPERATURE VARIATION OF THE CROSS-SECTION ABSORPTION BANDS OF OZONE IN THE 10000 TO 18500 CM^{-1} RANGE

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Two main absorption systems are covering the range observed : the Wulf and Chappuis bands.

A White absorption cell working at low temperature has been set up in the laboratory LASIM. It works from room until liquid nitrogen temperature. This cell was checked by comparison with a cell currently used until -50^{0}C at GSMA. The spectra were recorded with a Fourier Transform Spectrometer (Bomem DA03), at 4 cm^{-1} resolution for both cells in the region of Chappuis bands and the low temperature cell for the Wulf system.

When lowering the temperature the lineshape of the absorption profile evolves, improving the "bound-free" oscillation widths or the line overlap, clarifying the vibrational analysis of transitions [a]; in addition the low temperature cell allows measurement of cross-sections σ at temperatures lower than usually, closer of those which can happen sometimes in the high atmosphere.

For the seven main bands of the Wulf transition $^3A_2 \leftarrow X^1A_1$ the maximum of their absorption increases when lowering the temperature (9500-13000 cm^{-1}). For the main absorption in the Chappuis system ($\sim$ 14000-18500 cm^{-1}) it is generally admitted that σ does not vary with the temperature [b c]. On the contrary in our measurements σ decreases significantly when T decreases. Then in the transition region between the two systems (around 13500 cm^{-1}) σ does not vary significantly with T.

Our results at room temperature will be compared at excellent previous measurements such as those given in [d].

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[a] G. Wannous, A. J. Bouvier, Z. El Helou, X. Chillier, S. Churassy, A. Campargue, G. Weirauch, R. H. Judge, *Spectrochimica Acta A*, accepted for publication

[b] J. B. Burkhölder, R. K. Talukdar, *GeoPhys. Res. Lett.* **21**, 581-584 (1994).

[c] J. Orphal, *A Critical Review of the Absorption cross-section of O_3 and NO_2 in the 240-790 nm region; Part1. ozone (March 15, 2002). ESA Technical Note MO-TN-ESA-GO-0302*

[d] S. M. Anderson and K. Mauersberger *GeoPhys. Res. Lett.* **19**, 933-936 (1992).

INFRARED DIODE LASER SPECTROSCOPY OF THE CCO RADICAL: REGION OF THE C-C STRETCHING FUNDAMENTAL

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The CCO radical is postulated to act as an intermediate in a variety of chemical reactions and has been detected in space. In the past few years, our group has carried out infrared diode laser spectroscopy in the region of the C-O stretching fundamental (ν_1 band). Several rotationally resolved infrared bands of CCO were observed. These include the ν_1 fundamental and three hot bands in the ground electronic state ($X^3\Sigma^-$) as well as the ν_1 fundamental of the lowest lying metastable electronic state ($\tilde{a}^1\Delta$).

The detection of the C-C stretching fundamental (ν_3 band) is more challenging because the C-C stretching fundamental is much weaker and it occurs in a spectral region where much less sensitive detectors are used. In spite of these difficulties, we have measured the ν_3 and $2\nu_3 - \nu_3$ bands. For transitions with $N'' > 10$, each spectral line appears as a single line, indicating that the difference between the values of the spin-spin parameter in the upper and lower states in these bands is much smaller than those measured for the C-O stretching region.

The ν_3 band of the ($\tilde{a}^1\Delta$) state is predicted to occur in the same spectral region. The search for this band is currently underway. In this presentation, I will discuss the generation and detection of the CCO radical as well as some future directions.

A HIGH-RESOLUTION FAR-INFRARED GAS PHASE SPECTRUM OF THE INTERMOLECULAR HCl LIBRATION BAND OF THE OC-HCl COMPLEX

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The High-resolution far-infrared spectrum of the intermolecular libration band of OC-HCl has been recorded in a static multipass cell at 137 K, using a synchrotron radiation source. The rotational structure has been analyzed to yield a band origin at 201.20464 cm-1, the rotation constant, B', and quartic and sextic centrifugal distortion constants. The rotation constant and the centrifugal distortion constants have been used to obtain a Morse potential for the stretching of the intermolecular distance. The results are compared to results from CCSD(T) calculations.

Invited Lectures P

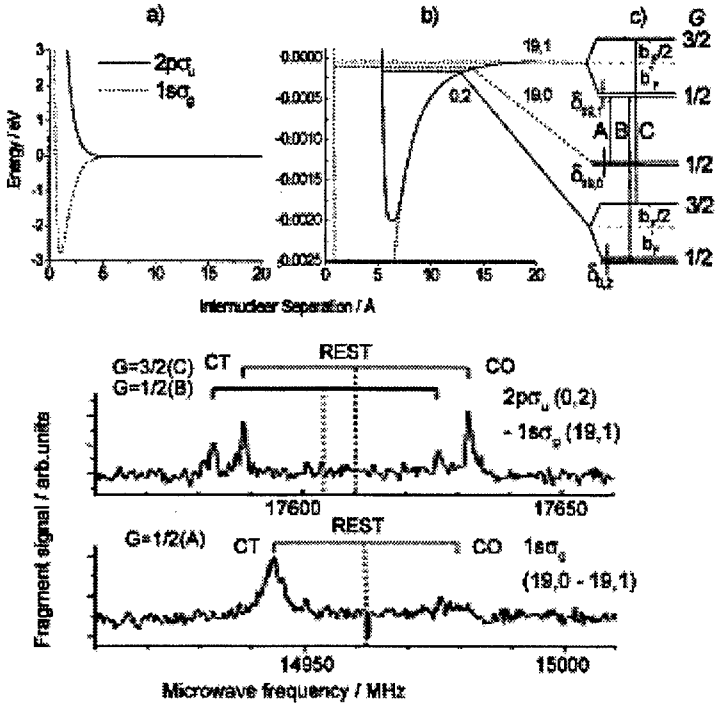
Friday, September 12, 14:00

Chairman : P. R. BUNKER

ORTHO-PARA TRANSITIONS IN H_2^+ *(45 min.)*

I. R. MCNAB, I. GERDOVA and F. KEMP, *Physics, University of Newcastle upon Tyne, UK NE1 7RU, United Kingdom*

Amongst the most strongly forbidden transitions in spectroscopy are those between adjacent rotational levels of a homonuclear diatomic molecule. We will briefly review how this selection rule arises as a result of ortho and para nuclear arrangements, and how it may be broken by nuclear hyperfine interactions. We will review ortho-para transitions observed by others before describing our recent measurement of a pure rotational transition bewteen the last two bound levels of the electronic ground state of H_2^+ [1,2]. In the figure below, (adapted from [1]) we show the relevant energy levels and spectra comparing an allowed microwave electronic transition (between the uppermost level of the ground electronic state and the 0,2 level of the first excited state) and a nearby forbidden pure rotation transition (between 19,0 and 19,1 of the ground electronic state). The allowed transition took 20 minutes to record, the forbidden transition required a weekend of signal averaging to record.



[1] Andrew D. J. Critchley, Alan N. Hughes and Iain R McNab *Phys. Rev. Lett.*, 86, 1725-1728 (2001).

[2] Andrew D.J. Critchley, Alan N. Hughes, Iain R. McNab and Richard E. Moss, *Molec. Phys.*, 101, 651-661 (2003).

SPECTRA OF WATER IN THE HEAVENS AND ON EARTH
(45 min.)

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Water is the third most common molecule in the Universe. The spectrum of water vapour is of fundamental importance for a variety of processes, including the absorption and retention of sunlight in Earth's atmosphere, combustion processes and atmospheres of cool stars. We have developed a complete and accurate predictive model for this spectrum. This uses first-principles calculations that approach experimental accuracy: variational nuclear motion calculations are combined with exceptionally large electronic structure calculations. These calculations consider a variety of effects, including failure of the Born-Oppenheimer approximation, relativistic effect and quantum electrodynamics, which have routinely been neglected in studies of small many-electron molecules.[a]

Studies of water spectra for astrophysical or atmospheric applications will discussed. These studies use a mixture of the completely *ab initio* procedure described above, and variational nuclear motion calculations based on the use of high accuracy, spectroscopically determined potentials.[b]

[a]O.L. Polyansky, A.G. Császár, S.V. Shirin, N.F. Zobov, P. Barletta, J. Tennyson, D.W. Schwenke and P.J. Knowles, *Science*, **299**, 539 (2003).

[b]S.V. Shirin, O.L. Polyansky, N.F. Zobov, P. Barletta and J. Tennyson, *J. Chem. Phys.*, **118**, 2124 (2003).

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L15, L17, L20, L28, L29, L30, L32, L36, L39, M1, M3, M4, M13, M15, M18, M23, M27, M29, M30, M32, N1, O4, O20, O21, O23, O24, O25, O30, O32, P1

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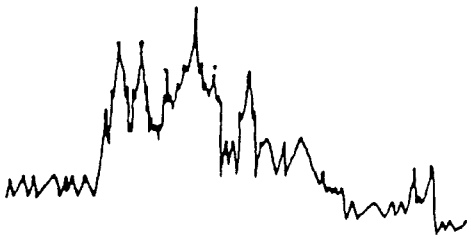

PRAHA2004

The 18th International Conference on High Resolution Molecular Spectroscopy
Prague, Czech Republic, September 5-9, 2004

The subjects covered at this meeting are largely identical to those covered at the Eighteenth Colloquium on High Resolution Molecular Spectroscopy. The first circular will be distributed by electronic mail in September 2003.

Information is available from the chairman of the local organizing committee

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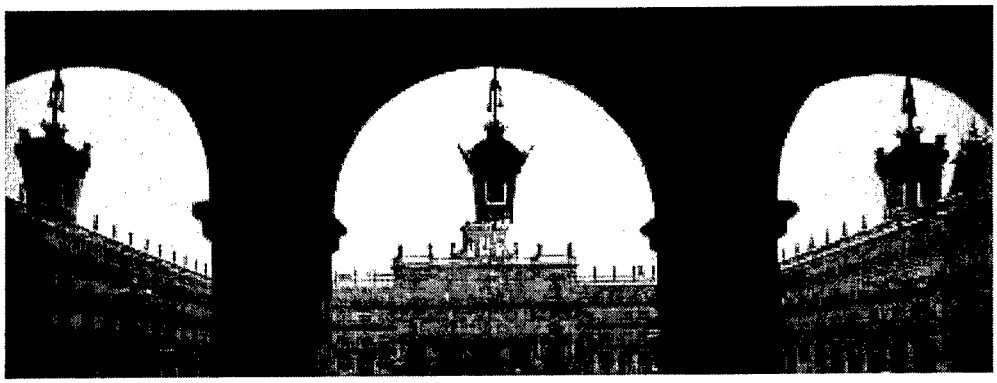
HIGH RESOLUTION MOLECULAR SPECTROSCOPY

19th Colloquium

Salamanca, Spain, 11-16 September 2005

Salamanca has the oldest University in Spain, and one of the oldest in Europe. The town was one of the European Cultural Capitals in 2002.



Colloquium web page (under construction):

http://www.iem.csic.es/hirms/congreso.htm

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BRUKER Optics

IFS 125HR

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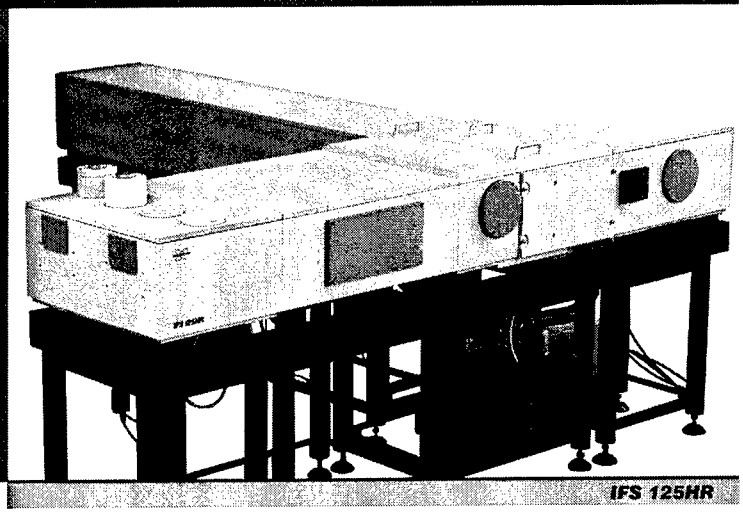
The new **IFS 125HR** FT-IR spectrometer is the successor to the established worldwide reference for high resolution measurements from the Far-IR to the UV, the *IFS 120HR*.



IFS 125HR

- Outstanding resolution across the entire spectrum.
- Resolved linewidths of $< 0.001\ cm^{-1}$
- Broad spectral range: from 5 cm^{-1} in the far-IR to >50,000 cm^{-1} in UV
- Double-sided interferogram acquisition up to 50cm OPD.
- Vacuum optics bench evacuable < 0.02 Torr
- Easy detector and range change

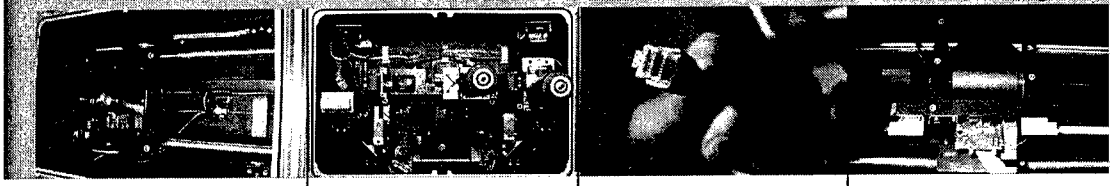
The Bruker Optics ***IFS 125HR*** FT-IR spectrometer offers the highest resolution available over a wide wavelength range from 5 cm^{-1} in the Far-IR to 50,000 cm^{-1} in the UV.

The scanner allows collection of data at very high resolution without beam folding. With the improved electronics, free running delta-sigma 24 bit ADC and Ethernet TCP/IP connectivity, the ***IFS 125HR*** provides the performance that any demanding application may need. Automatic detector-, beamsplitter- and accessory recognition assists the user in setting-up experiments.

Studies of physical-chemical primary processes of chemical reactions require very high spectral resolution to derive the true molecular quantum motion from the absorption spectra. In addition, high resolution FT-IR spectroscopy is ideal for investigating changes in stratospheric gas concentrations due to its sensitivity and selectivity. Some applications:

- Structure analysis of gaseous molecules at low pressure
- Low temperature measurements on solids
- Emission of high temperature gasses
- Environmental atmosphere analysis

innovative, intuitive, intelligent



Longer bearing assemblies can be substituted to achieve higher resolution.

Up to 4 internal and 2 external detectors can be mounted on the IFS 125HR.

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