

SIXTEENTH COLLOQUIUM ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY

Université de Bourgogne

DIJON

6 - 10 September 1999

Programme and Abstracts



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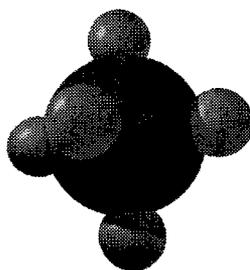
The Sixteenth Colloquium on High Resolution
Molecular Spectroscopy

DIJON 99

6-10 September 1999

Université de Bourgogne

DIJON - FRANCE



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The Sixteenth Colloquium on High Resolution Molecular Spectroscopy

DIJON 1999

6-10 September 1999

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DIJON 99 – COLLOQUIUM PROGRAM

DATES	06/09/1999	07/09/1999	08/09/1999	09/09/1999	10/09/1999
Hours	Monday	Tuesday	Wednesday	Thursday	Friday
9:00	Inv. speakers A +	Inv. speakers E +	Inv. speakers I +	Inv. speakers K +	Inv. speakers N +
11:00 – 12:30	Poster Session B	Poster Session F	Poster Session J	Poster Session L	Poster Session O
	Lunch†	Lunch†	Lunch†	Lunch†	Lunch†
14:00	Inv. speakers C +	Inv. speakers G +	<u>Departure 13:30</u>	Free afternoon	Inv. speakers P
16:00 – 17:30	Poster session D	Poster session H	Sight seeing tour	Dinner†	
	Dinner†	Town Hall reception			
Evening			Banquet	Poster session M	

† Please note : There will be free access to the restaurant from 11:20 to 13:30 for lunch and from 18:30 to 19:30 for dinner.

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Program of Sessions

Invited Lectures A, Monday, September 6, 9:00

Chairman : M. QUACK

A1 - *INFRARED CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY*R.J. SAYKALLYA2 - *NEW DEVELOPMENTS OF INTRACAVITY ABSORPTION SPECTROSCOPY: APPLICATION TO THE CH ACETYLENIC OVERTONE TRANSITIONS OF PROPYNE*A. CAMPARGUE**Poster Session B, Monday, September 6, 11:00**B1 - *CW-DIODE-LASER CAVITY-RING-DOWN SPECTROSCOPY OF NITROUS OXIDE AND METHANE IN PULSED SUPERSONIC SLIT JETS*
MICHAEL HIPPLER, and MARTIN QUACKB2 - *CAVITY RING-DOWN SPECTROSCOPY WITH MID-INFRARED CW LASERS FOR ATMOSPHERIC TRACE GAS DETECTION*M. MÜRTZ, H. DAHNKE, D. KLEINE, S. STRY, P. HERING and W. URBANB3 - *JET-DISCHARGE CAVITY RINGDOWN SPECTROSCOPY OF IONIZED POLYCYCLIC AROMATIC HYDROCARBONS: PROGRESS IN TESTING THE PAH HYPOTHESIS FOR THE DIFFUSE INTERSTELLAR BAND PROBLEM*D. ROMANINI, L. BIENNIER, A. KACHANOV, F. STOECKEL, F. SALAMA, and L. J. ALLAMANDOLAB4 - *HIGH RESOLUTION PHOTOACOUSTIC AND FTIR OVERTONE SPECTRA OF DIACETYLENE*OLAVI VAITTINEN, MARKUS METSÄLÄ, MARIA SAARINEN, LAURI HALONEN, WOLFGANG JERZEMBECK, and HANS BÜRGERB5 - *SPECTROSCOPIC INVESTIGATION OF VIBRATION-ROTATION BANDS IN ACETALDEHYDE: FOCUS ON ν_3 ($n=1-5$) ALDEHYDE CH STRETCH BANDS*M. HERMAN, F. HERREGODTS, R. GEORGES, M. HEPP, I. HADJ BACHIR, M. LECOUTRE, and I. KLEINERB6a - *FAST PHASE-SELECTIVE DETECTION OF TRANSIENT SPECIES WITH STEP-SCAN FOURIER TRANSFORM SPECTROSCOPY*NATHALIE PICQUÉ and GUY GUELACHVILIB6b - *DOPPLER-SHIFT MEASUREMENTS AND INVESTIGATION OF THE STATE-TO-STATE DEPENDENCE OF THE ArH^+ ION AVERAGE MOBILITY IN A Ar/He PLASMA*NATHALIE PICQUÉ

- B7 - ROVIBRATIONAL ANALYSIS OF THE ν_6 BANDS OF FOUR ISOTOPO-
MERS OF FCIO_3
G. GRANER, F. MEGUELLATI, A. CEASU, K. BURCZYK, G. PAWELKE,
and P. PRACNA
- B8 - THE $\nu_6=2$ STATES OF FCIO_3
G. GRANER, K. BURCZYK and H. BÜRGER
- B9 - SUB-DOPPLER POLARIZATION SPECTROSCOPY OF THE $B^1\Pi_u \leftarrow$
 $X^1\Sigma_g^+$ SYSTEM FOR Cs_2 WITH A TITANIUM SAPPHIRE LASER
NOBUO NISHIMIYA, TOKIO YUKIYA, and MASAO SUZUKI
- B10 - HIGH - RESOLUTION LASER SPECTROSCOPY OF THE $A^3\Pi_1 \leftarrow X^1\Sigma^+$
SYSTEM OF IBr WITH A TITANIUM:SAPPHIRE RING LASER
TOKIO YUKIYA, NOBUO NISHIMIYA and MASAO SUZUKI
- B11 - DIODE-LASER MEASUREMENTS OF N_2 -BROADENING
COEFFICIENTS IN THE ν_7 BAND OF C_2H_4
J. WALRAND, G. BLANQUET, and J.-P. BOUANICH
- B12 - HIGH RESOLUTION SPECTRA OF CARBON DISULFIDE $^{12}\text{C}^{32}\text{S}_2$ IN
THE REGION OF $2 \mu\text{m}$
Gh. BLANQUET, M. LENGELÉ, J. WALRAND, H. BREDOHL,
and I. DUBOIS
- B13 - THE GROUND STATE ROTATIONAL SPECTRA OF H_2^{13}CO AND $\text{H}_2\text{C}^{18}\text{O}$
H. S. P. MÜLLER, G. WINNEWISSER, U. WÖTZEL, H. MÄDER,
R. BOCQUET, and J. DEMAISON
- B14 - THE $\nu_3 = 1$ STATE OF HSiF_3 AND DSiF_3 STUDIED BY HIGH RESO-
LUTION INFRARED AND MILLIMETERWAVE SPECTROSCOPY
E.B. MKADMI, H. BÜRGER, L. MARGULÉS, M. GNIDA
and J. DEMAISON
- B15 - ROVIBRATIONAL SPECTROSCOPY OF THE $\nu_5=1$ LEVEL OF $^{28}\text{SiDF}_3$
P. PRACNA, L. MARGULES, J. COSLÉOU, J. DEMAISON, E. B. MKADMI,
and H. BÜRGER
- B16 - ROTATIONAL ANALYSIS OF THE ν_2 BAND OF DIAZIRINE- d_2 FROM
HIGH RESOLUTION FTIR SPECTRA
A. GAMBI, and P. STOPPA
- B17 - FTIR SPECTROSCOPY OF BrCN ISOTOPOMERS IN THE REGION OF
THE $2\nu_3$ BAND: AN IMPROVED EVALUATION OF THE ANHARMONIC
FORCE FIELD OF CYANOGEN BROMIDE
L. BIZZOCCHI, C. DEGLI ESPOSTI, and G. D. NIVELLINI
- B18 - EXTREMELY HIGH ROTATIONAL EXCITATION OF CO IN A DIS-
CHARGE THROUGH COLD CO
CLAUDINA COSSART-MAGOS and DANIEL COSSART

- B19 - *A PRELIMINARY STUDY IN CH_3SiD_3 OF THE HOT BAND ($\nu_{12} = 1, \nu_6 = 1$) \leftarrow ($\nu_{12} = 0, \nu_6 = 1$)*
J. SCHRODERUS, V.-M. HORNEMAN, I. OZIER,
and N. MOAZZEN-AHMADI
- B20 - *MEASUREMENTS OF ROTATIONAL TRANSITIONS OF RARE CO ISOTOPOMERS*
G. KLAPPER, F. LEWEN, G. WINNEWISSER, and S. P. BELOV
- B21 - *COLLISION-INDUCED ABSORPTION BANDSHAPES IN O_2 AND CO_2 : INTERPLAY OF LINE-MIXING EFFECT AND VAN DER WAALS ASSOCIATION*
A. A. VIGASIN
- B22 - *ARE FREQUENCY LINESHIFTS ADDITIVE ? THE AMMONIA SPECTRUM AS AN EXPERIMENTAL TEST OF THE RYDBERG-RITZ PRINCIPLE*
M. IBRAHIMI, B. LEMOINE and F. ROHART
- B23 - *AIR-BROADENING AND SHIFT COEFFICIENTS AND LINE MIXING IN THE ν_3, ν_5 , AND ν_6 BANDS OF $^{12}\text{CH}_3\text{D}$*
M. A. H. SMITH, C. P. RINSLAND, V. MALATHY DEVI, and D. CHRIS BENNER
- B24 - *LINE MIXING IN WATER VAPOR SPECTRUM: NON-LINEAR PRESSURE SHIFTS IN THE $\nu_2 + \nu_3$ BAND*
BYKOV A.D., LAVRENTIEVA N.N., SINITSA L.N., and SOLODOV A.M
- B25 - *HIGH RESOLUTION FTIR INVESTIGATION ON THE 1,3,5-TRIAZINE ISOTOPOMER $\text{C}_3^{15}\text{N}_3\text{D}_3$*
J. MARTZ, and A. RUOFF
- B26 - *LINE POSITIONS OF PHOSPHINE IN THE $3 \mu\text{m}$ REGION FOR PLANETARY SPECTRA ANALYSIS*
L. R. BROWN, I. KLEINER, and C. COTTAZ
- B27 - *FAST SCAN SUBMILLIMETER SPECTROSCOPIC TECHNIQUE (FASST): SPECTROSCOPIC AND ANALYTICAL APPLICATIONS*
SIEGHARD ALBERT, and FRANK C. DE LUCIA
- B28 - *DIFFERENTIAL UV SPECTROSCOPIC STUDIES OF Ag^+ INTERACTION WITH NATURAL DNA AND NUCLEOTIDES*
IRINA V. SYSA, VICTOR A. SOROKIN, VLADIMIR A. VALEEV,
GALINA O. GLADCHENKO, MARINA V. DEGTYAR,
and YURI P. BLAGOI
- B29 - *COMPETITION BETWEEN ORBITAL ANGULAR MOMENTUM AND VIBRATIONAL RESONANCE EFFECTS IN THE SPECTRUM OF NH_2*
ALEXANDER ALIJAH, and GEOFFREY DUXBURY
- B30 - *SPECTROSCOPY IN THE VUV RANGE AT A RESOLUTION OF 0.01 cm^{-1}*
U. HOLLENSTEIN, and F. MERKT

- B31 - ANALYSIS OF THE FOURIER TRANSFORM EMISSION SPECTRA OF NH_2 IN THE 6 000-10 000 cm^{-1} REGION
NICOLAS NÉEL, LAURENT H. COUDERT, and MICHEL VERVLOET
- B32 - THE ν_1 AND ν_2 BANDS OF AR-HN_2^+ : AN EXAMPLE OF AN EXCEPTIONAL VIBRATIONAL ANHARMONICITY
P. BOTSCHWINA, R. OSWALD, H. LINNARTZ, D. VERDES,
and J.P. MAIER
- B33 - MILLIMETER WAVE INTRACAVITY JET SPECTROMETER FOR STUDY OF WEAKLY BOUND MOLECULAR COMPLEXES
I. PAK, L. A. SURIN, B. S. DUMESH, F. LEWEN, D. ROTH, and G. WINNEWISSER
- B34 - ROTORSIONAL SPECTRA OF $(\text{CH}_3)_3\text{X}-\text{Y}$ TYPE MOLECULES
I. MERKE, A. WELZEL, W. STAHL, S. KASSI, D. PETITPREZ,
and G. WLODARCZAK
- B35 - MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF VINYL-STIBINE
S. KASSI, D. PETITPREZ, G. WLODARCZAK, S. EL CHAOUCH
and J.C. GUILLEMIN
- B36 - A NONADIABATIC FRANCK-CONDON CALCULATION OF THE $\tilde{\text{A}}^2\text{B}_2 \leftarrow \tilde{\text{X}}^2\text{A}_1$ ABSORPTION SPECTRUM OF NO_2
M. JACON and D. BELMILOUD
- B37 - THE DENSITY MATRIX OF $\text{H}_2\text{O} - \text{N}_2$ IN THE COORDINATE REPRESENTATION: A MONTE CARLO CALCULATION OF THE FAR-WING LINE SHAPE
Q. MA, and R. H. TIPPING
- B38 - INFRARED SPECTROSCOPY ON THE LOWEST TRIPLET STATE OF THE PYRAZINE-ARGON COMPLEX USING A FREE ELECTRON LASER
KAREN REMMERS, ROB SATINK, GERT VON HELDEN, HANS PIEST, GERARD MEIJER, and W. LEO MEERTS
- B39 - ANALYTICAL APPROXIMATION FOR ADIABATIC CORRECTION, NONADIABATIC MATRIX ELEMENTS AND TRANSITION MOMENTS OF RYDBERG DIATOMIC STATES IN QUANTUM DEFECT THEORY. APPLICATION TO $s, d^3\Sigma_g^+$ STATES OF HYDROGEN MOLECULE
A.V. STOLYAROV, and M.S. CHILD
- B40 - MOLECULAR ANHARMONICITY - A COMPUTER AIDED TREATMENT
R. G. DELLA VALLE, L. HALONEN, and E. VENUTI

Invited Lectures C, Monday, September 6, 14:00

Chairman : J.-P. CHAMPION

- C1 - *REDUCTIONS-A WAY HOW TO DETERMINE UNAMBIGUOUS SPECTROSCOPIC CONSTANTS WITH A CLEAR PHYSICAL MEANING*
KAMIL SARKA
- C2 - *GLOBAL ROVIBRATIONAL ANALYSIS OF LINEAR MOLECULES*
A. FAYT

Poster Session D, Monday, September 6, 16:00

- D1 - *GLOBAL ROVIBRATIONAL ANALYSIS OF HCCNC BASED ON NEW INFRARED AND SUBMILLIMETER-WAVE SPECTRA*
C. VIGOUROUX, A. FAYT, H. BÜRGER, A. GUARNIERI, A. HUCKAUF,
D. LENTZ and C. BARTEL
- D2 - *GLOBAL FITTINGS OF ROVIBRATIONAL LINE POSITIONS OF NITROUS OXIDE*
V.I. PEREVALOV, S.A. TASHKUN, and J.-L. TEFFO
- D3 - *THE $2\nu_1 + 5\nu_3$ TRIADS OF $^{12}\text{C}^{16}\text{O}_2$ AND $^{13}\text{C}^{16}\text{O}_2$: OVERTONE SPECTROSCOPY AND COMPARISON WITH A GLOBAL ANALYSIS OF THE VIBRATION - ROTATION STRUCTURE*
S. A. TASHKUN, V.I. PEREVALOV, J.-L. TEFFO, D. BAILLY,
M. LECOUTRE, T.R. HUET, G. WEIRAUCH, A. CAMPARGUE, and M.P. ESPLIN
- D4 - *VIBRATIONAL POLYADS IN C_2H_2 . INTER-POLYAD AND INTRA-POLYAD STRUCTURE*
M. I. EL IDRISSE, J. LIEVIN, N. VAECK, M. HERMAN,
and B. ZHILINSKII
- D5 - *THE INTENSITIES OF METHANE IN THE 3 TO 5 μm REGION REVISITED*
L. FEJARD, J.P. CHAMPION, J.M. JOUVARD, L.R. BROWN, and A. PINE
- D6 - *ABSOLUTE LINE INTENSITIES IN THE $2\nu_2^0$ BAND OF $^{35}\text{ClCN}$ AND $^{37}\text{ClCN}$ AT 12.8 μm*
M. LEPERE, Gh. BLANQUET and J. WALRAND
- D7 - *CAVITY RING DOWN SPECTROSCOPY (CRDS) OF NO_2 IN THE NEAR INFRARED REGION : ANALYSIS OF THE $\tilde{X}^2\text{A}_1$ - $\tilde{\text{A}}^2\text{B}_2$ CONICAL INTERSECTION*
RÉMY JOST, PATRICE THEULÉ, SYLVAIN HEILLIETTE, ANTOINE DELON, and PATRICK DUPRÉ

- D8 - HIGH RESOLUTION CW CAVITY RING DOWN SPECTROSCOPY (CRDS) FOR PROBING WEAK MOLECULAR TRANSITIONS: UNEXPECTED NONLINEAR TRANSITIONS IN JET-COOLED NO_2
S. HEILLIETTE, R. JOST, A. DELON, D. ROMANINI and P. DUPRÉ
- D9 - SPECTROSCOPY OF XY_5Z (C_{4v}) SYMMETRIC TOP MOLECULES : A TENSORIAL FORMALISM ADAPTED TO THE $O(3) \supset O_h \supset C_{4v}$ CHAIN
M. ROTGER, V. BOUDON and M. LOËTE
- D10 - TRANSITION MOMENTS FOR XY_5Z (C_{4v}) SYMMETRIC TOP MOLECULES USING THE TENSORIAL FORMALISM
M. ROTGER, V. BOUDON and M. LOËTE
- D11 - HIGH RESOLUTION FTIR AND PHOTOACOUSTIC OVERTONE SPECTRA OF HCCCl
MARIA SAARINEN, KIRSI NISKANEN, LAURI HALONEN,
HANS BÜRGER and OLIVER POLANZ
- D12 - INVESTIGATION OF H_2O OVERTONES BY LASER INDUCED FLUORESCENCE
MARIA SAARINEN, DMITRI PERMOGOROV and LAURI HALONEN
- D13 - CAVITY RING DOWN SPECTROSCOPY ON CARBON CHAIN RADICALS
T. MOTYLEWKI, O. VAIZERT, and H. LINNARTZ
- D14 - TUNABLE FAR INFRARED SPECTROSCOPY OF $^X\text{KRH}^+$ AND $^X\text{KRD}^+$ ($X=82,84,86$)
H. ODASHIMA, F. MATSUSHIMA, A. KOZATO, S. TSUNEKAWA, K. TAKAGI, L.R. ZINK, K.M. EVENSON, and H. LINNARTZ
- D15 - MICROWAVE SPECTROSCOPY OF 1-CHLORO-1,1-DIFLUOROETHANE
V. V. ILYUSHYN, E. A. ALEKSEEV, O. I. BASKAKOV, and S. F. DYUBKO
- D16 - MILLIMETER-WAVE SPECTRUM OF CF_2Cl_2
O. I. BASKAKOV, S. F. DYUBKO, A. A. KATRICH, V. V. ILYUSHYN and E. A. ALEKSEEV
- D17 - WIDE-RANGE MILLIMETER-WAVE SPECTROMETER
E. A. ALEKSEEV and V. V. ILYUSHYN
- D18 - INFLUENCE OF THE COLLISION PARTNER (He AND Ar) ON LINE-MIXING EFFECTS IN THE ν_3 INFRARED BAND OF METHANE AT ROOM TEMPERATURE
D. PIERONI, NGUYEN-VAN-THANH, C. BRODBECK, J.-M. HARTMANN,
T. GABARD, J.-P. CHAMPION, D. BERMEJO, J.-L. DOMENECH,
C. CLAVEAU, A. VALENTIN, M. V. TONKOV, I. M. GRIGORIEV, and R. Le DOUCEN
- D19 - THE MILLIMETER- AND SUBMILLIMETER-WAVE SPECTRUM AND THE DIPOLE MOMENT OF ETHYLENIMINE, $c\text{-C}_2\text{H}_4\text{NH}$
SVEN THORWIRTH, HOLGER S. P. MÜLLER,
and GISBERT WINNEWISSER

- D20 – *SUB-DOPPLER MEASUREMENTS ON THE ROTATIONAL TRANSITIONS OF HYDROGEN CYANIDE*
V. AHRENS, F. LEWEN, and G. WINNEWISSER
- D21 – *A HIGH RESOLUTION INFRARED STUDY OF THE NASCENT NO PRODUCED IN THE REACTION $\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$*
MARCEL SNELS, ROBERTA FANTONI, MARIANO GIORGI, MICHELE ALAGIA, and PIERGIORGIO CASAVECCHIA
- D22 – *SUB-DOPPLER DIODE LASER JET SPECTROSCOPY OF FREONS*
MARCEL SNELS, LUCA PICCARRETA, and ANNA-MARIA SANTORO
- D23 – *TEMPERATURE DEPENDENCES OF PRESSURE-BROADENING, PRESSURE-SHIFTING AND LINE MIXING DUE TO AIR IN THE ν_3 BAND REGION OF $^{12}\text{CH}_4$*
V. MALATHY DEVI, D. CHRIS BENNER, MARY ANN H. SMITH, CURTIS P. RINSLAND, GUY GUELACHVILI, NATHALIE PICQUÉ, and LINDA R. BROWN
- D24 – *PROGRESS IN HIGH-INFORMATION TIME-RESOLVED FOURIER TRANSFORM SPECTROSCOPY*
NATHALIE PICQUÉ and GUY GUELACHVILI
- D25 – *PRECISE LINE STRENGTHS AND BROADENING PARAMETERS FOR THE $2\nu_1 + 2\nu_2^0 + \nu_3$ COMBINATION BAND OF CO_2 AROUND 1575 nm BY DIODE LASER SPECTROSCOPY*
J. HENNINGSEN
- D26 – *WATER VAPOR LINE PARAMETERS IN THE 3500-3650 cm^{-1} REGION*
KAREN KEPPLER ALBERT, D. CHRIS BENNER, V. MALATHY DEVI, MARY ANN H. SMITH, and MICHAEL LOCK
- D27 – *ON THE NEW HIGH RESOLUTION STUDY OF THE ROTATIONAL STRUCTURES OF THE AsH_3 VIBRATIONAL STATES (0200), (0101), AND (0002)*
O.N. ULENIKOV, G.A. ONOPENKO, O.L. PETRUNINA, J. SCHRODERUS, S. ALANKO, and R. ANTTILA
- D28 – *THE GROUND AND FIRST TORSIONAL STATES OF DEUTERATED ACETALDEHYDE: LINE POSITION AND HYPERFINE STRUCTURE ANALYSES*
I. KLEINER, L. H. COUDERT, J. C. LOPEZ, S. BLANCO, A. R. W. McKELLAR, and N. MOAZZEN-AHMADI
- D29 – *GENERALIZED SIMULATED ANNEALING METHOD IN THE ANALYSIS OF ATOM-ATOM INTERACTION*
R. F. GUTTERRES, C. FELLOWS, O. DULIEU, and M. ARGOLLO DE MENEZES
- D30 – *IODINE ATLAS AS FREQUENCY REFERENCE ONLINE*
B. BODERMANN, M. FRANK, H. KNÖCKEL, and E. TIEMANN

- D31 - *THE APPARENT DISORDER OF THE Rb_2 $A^1\Sigma_u^+(0_u^+) \sim b^3\Pi_u(0_u^+)$ SPECTRUM RESOLVED: A CASE OF FULLY COUPLED ELECTRONIC STATES*
CLAUDE AMIOT, OLIVIER DULIEU, VIATCHESLAV KOKOULINE, and JEAN VERGÈS
- D32 - *IR SPECTRA OF THE OPEN SHELL IONIC COMPLEXES $H_2O^+ - Rg_n$*
O. DOPFER, D. ROTH, and J. P. MAIER
- D33 - *EFFECTS OF ELECTRON-SPIN ON THE INFRARED SPECTRUM OF THE O_2 -HF COMPLEX*
WAFAA M. FAWZY, and CHRIS LOVEJOY
- D34 - *THE HIGH RESOLUTION INFRARED SPECTRUM OF THE WEAKLY-BOUND VAN DER WAALS COMPLEX N_e-CH_4 IN THE $7\mu m$ REGION ($j=1 \leftarrow 0$ TRANSITIONS)*
M. WANGLER, D.A. ROTH, I. PAK, G. WINNEWISSER, D. SCOUTERIS and B.J. HOWARD
- D35 - *OBSERVATION OF THE ν_3 FUNDAMENTAL BAND OF $HBBr^+$*
D. COLLET, N.T. HUNT, Z. LIU and P.B. DAVIES
- D36 - *EXCITATION SPECTROSCOPY OF THE F_eF RADICAL*
STEPHEN M. KERMODE and JOHN M. BROWN
- D37 - *ON THE EQUILIBRIUM STRUCTURE AND DIPOLE MOMENT OF CIS-1-CHLORO-2-FLUOROETHYLENE*
A. GAMBI, G. CAZZOLI, L. DORE, A. MAZZAVILLANI, and C. PUZZARINI
- D38 - *MODE SELECTIVE STEREOMUTATION AND INVERSION IN ANILINE: HIGH RESOLUTION INFRARED SPECTROSCOPY AND 36-DIMENSIONAL HAMILTONIAN APPROACH*
BENJAMIN FEHRENSSEN, DAVID LUCKHAUS and MARTIN QUACK
- D39 - *THE VIBRATIONAL-ROTATIONAL ENERGY LEVELS OF SILANONE*
JACEK KOPUT, STUART CARTER, and NICHOLAS C. HANDY
- D40 - *MOLECULAR SPECTROSCOPY OF PHASE TRANSITIONS IN LIQUID CRYSTALS*
VALERIJ POGORELOV, VYACHESLAV BUKALO, and YURI ASTASHKIN

Invited Lectures E, Tuesday, September 7, 9:00

Chairman : L. ROTHMAN

- E1 - *SPECTROSCOPY OF NEARLY-DISSOCIATING MOLECULES*
ALAN CARRINGTON
- E2 - *HIGH RYDBERG STATES AND HIGH RESOLUTION SPECTROSCOPY*
F. MERKT

Poster Session F, Tuesday, September 7, 11:00

- F1 - *HIGH RESOLUTION PFI-ZEKE PHOTOELECTRON SPECTROSCOPY OF THE FIRST ELECTRONIC STATES OF KR₂⁺*
U. HOLLENSTEIN, R. SIGNORELL, and F. MERKT
- F2 - *m_j-PREFERENTIAL PREDISSOCIATION IN THE D¹Σ_u⁺ STATE OF THE Cs₂ MOLECULE*
M. BABA, Y. KIMURA, S. KASAHARA, and H. KATO
- F3 - *VUV PHOTODISSOCIATION PATHWAYS OF C₂H₂ VIA RYDBERG STATES STUDIED WITH SYNCHROTRON RADIATION*
A. CAMPOS, S. BOYÉ, Ph. BRÉCHIGNAC, S. DOUIN, C. FELLOWS, N. SHAFIZADEH, and D. GAUYACQ
- F4 - *RESONANT 2-PHOTON IONIZATION STUDY of AlND₃ COMPLEX: EXCITED ELECTRONIC STATES*
ZYGMUNT J. JAKUBEK and BENOIT SIMARD
- F5 - *PHOTOASSOCIATION SPECTROSCOPY OF THE PURE LONG-RANGE STATES IN Cs₂*
CLAUDE AMIOT, DANIEL COMPARAT, ANNE CRUBELLIER, CYRIL DRAG, OLIVIER DULIEU, ANDREA FIORETTI, BRUNO LABURTHE, FRANCOISE MASNOU-SEEUWS, and PIERRE PILLET
- F6 - *ULTRA-HIGH RESOLUTION SPECTROSCOPY IN THE INFRARED REGION USING A SUPERSONIC BEAM OF SF₆*
A. AMY-KLEIN, L.F. CONSTANTIN, R.J. BUTCHER, P.E. DURAND and Ch. CHARDONNET
- F7 - *STRIKING ANHARMONIC RESONANCES IN N₂O₄: SUPERSONIC JET FOURIER TRANSFORM SPECTRA AT 13.3, 7.9, 5.7 AND 3.2 μm*
MARTIN HEPP, ROBERT GEORGES, MICHEL HERMAN, JEAN-MARIE FLAUD, and WALTER J. LAFFERTY
- F8 - *FTIR SPECTROSCOPY IN A SUPERSONIC LAVAL NOZZLE*
ROBERT GEORGES, ABDESSAMAD BENIDAR, ROGER Le DOUCEN, and JOËL BOISSOLES
- F9 - *HIGH RESOLUTION INFRARED SPECTROSCOPIC STUDY OF THE ν₃ BAND OF ReF₆ IN A SUPERSONIC JET EXPANSION*
V. BOUDON, M. ROTGER, Y. HE, H. HOLLENSTEIN, M. QUACK and U.SCHMITT
- F10 - *SPONTANEOUS RAMAN SPECTROSCOPY OF CLOSED AND OPEN-SHELL TRANSITION-METAL FLUORIDES*
M. ROTGER, M. REY, V. BOUDON, M. LOËTE, A. LORRIAUX, and H. SELIG
- F11 - *ROTATIONAL SPECTRA OF THE 3ν₁₈, ν₁₁+ν₁₈, AND ν₁₇ VIBRATIONAL STATES OF CF₃CFH₂*

- V. V. ILYUSHYN, E. A. ALEKSEEV, O. I. BASKAKOV,
and S. F. DYUBKO
- F12 – *THE WATER VAPOR CONTINUUM IN THE MMW REGION. THE ROLE OF VARIOUS MIXING GASES*
M. GODON, A. BAUER, and R.R. GAMACHE
- F13 – *THE EFFECT OF PULSED MAGNETIC, RF AND ELECTRIC FIELDS ON MOLECULAR COHERENCES STUDIED WITH QUANTUM BEAT SPECTROSCOPY*
ROBERT T. CARTER, HUBERTUS RING and J. ROBERT HUBER
- F14 – *THE STRETCHING FUNDAMENTALS OF SbD₃*
E. CANÉ, L. FUSINA, H. BÜRGER, and W. JERZEMBECK
- F15 – *ANALYSIS OF HIGH RESOLUTION SPECTRA OF ¹⁸O₃ IN THE REGION 1600-1900 cm⁻¹*
A. CHICHERY, A. BARBE and J.J. PLATEAUX
- F16 – *COMPLETE ANALYSIS OF THE TETRAD (003)/(102)/(201)/(300) INTERACTING STATES OF ¹⁶O₃ MOLECULE*
S. MIKHAILENKO, A. BARBE, VI.G. TYUTEREV, and J.J. PLATEAUX
- F17 – *THE HIGH-RESOLUTION INFRARED SPECTRUM OF THE SYMMETRY FORBIDDEN BAND, ν_5 , OF ¹⁰B₂H₆*
J.-M. FLAUD, W.J. LAFFERTY, H. BÜRGER, and G. PAWELKE
- F18 – *ROTATIONAL ANALYSIS OF THE ν_7 BAND IN FURAN (C₄H₄O)*
A. MELLOUKI, M. HERMAN, and B. LEMOINE
- F19 – *HIGH RESOLUTION INFRARED SPECTROSCOPY OF SMALL CARBON CLUSTERS*
U. BERNDT, G. FUCHS, T. GIESEN, and G. WINNEWISSER
- F20 – *RITZ ASSIGNMENT AND AWAT FIT OF THE RING-PUCKERING HOT BANDS OF OXETANE*
GIOVANNI MORUZZI, MARC KUNZMANN, BRENDA P. WINNEWISSER
and MANFRED WINNEWISSER
- F21 – *PRECISION MEASUREMENTS OF ETHYLENE AND ISOTOPIC ETHYLENE ¹³C¹²CH₄ SPECTRAL LINES NEAR 10.5 μ m BY THE INFRARED HETERODYNE SPECTROMETER*
T. KOSTIUK, D. BUHL, T. HEWAGAMA, T. A. LIVENGOOD,
V. MOROZHENKO, and A. KOLLYUKH
- F22 – *LINE MIXING IN IR SPECTRA OF INTEREST FOR ATMOSPHERIC RADIATIVE TRANSFER*
C. B. SUAREZ, D. C. REUTER, and M. J. SIROTA
- F23 – *LINE BROADENING OF THE 551.5 GHz LINE OF NO PERTURBED BY N₂ and O₂*
J.-M. COLMONT, J.-F. d'EU, F. ROHART, and G. WLODARCZAK

- F24 - INVESTIGATION OF J-DEPENDANCE OF LINE BROADENING AND LINE SHIFT IN THE $\nu_1+3\nu_3$ BAND OF ACETYLENE PERTURBED BY He, Ne, Ar AND AIR
H. VALIPOUR, and D. ZIMMERMANN
- F25 - ISOTOPOMER DEPENDENCE OF N₂- AND O₂-BROADENED HALF-WIDTHS OF WATER VAPOR TRANSITIONS
R. R. GAMACHE
- F26 - SELF-ASSOCIATION OF THE XANTHINE MOLECULES AS STUDIED BY FTIR SPECTROSCOPY, FACTOR ANALYSIS AND SEMIEMPIRICAL QUANTUM MECHANICS
I. KUZMANOVSKI, M. TRPKOVSKA, B. SOPTRAJANOV, LJ. PEJOV, and V. STEFOV
- F27 - A COMPACT MILLIMETER WAVE SPECTROMETER IN THE 50 - 110 GHZ REGION
I. MERKE
- F28 - ANALYSIS OF THE OCTAD SYSTEM OF ¹²CH₄
J.-C. HILICO, O. ROBERT, M. LOETE, S. TOUMI, A.S. PINE, and L.R. BROWN
- F29 - THE SET OF VALLEY RIDGE INFLECTION POINTS ON THE POTENTIAL ENERGY SURFACE OF WATER
W. QUAPP, M. HIRSCH, and D. HEIDRICH
- F30 - HIGH-RESOLUTION MEASUREMENTS OF LINE AND BAND OS STRENGTHS IN THE DIPOLE-ALLOWED ABSORPTION SPECTRUM OF ¹⁴N₂
M.-C. CHAN, K. P. HUBER, K. ITO, T. MATSUI, and G. STARK
- F31 - THE INFLUENCE OF AN EXTERNAL MAGNETIC FIELD ON THE SCATTERING LENGTH OF Na
T. LAUE, C. SAMUELIS, H. KNÖCKEL, and E. TIEMANN
- F32 - LIFTETIMES OF THE LOWEST ELECTRONICALLY EXCITED STATES ³A₂ AND ³B₂ OF OZONE
UWE WACHSMUTH, SABINE F. DEPPE, ALES CHARVAT, and BERND ABEL
- F33 - ISOMERS AND MICROSOLVATION IN SiOH⁺-Ar_n COMPLEXES (n=1-10)
O. DOPFER, R. V. OLKHOV, and S. A. NIZKORODOV
- F34 - FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF THE WEAKLY BOUND DIMER N₂-IH
WOLFGANG JABS, AVERY McINTOSH, ROBERT R. LUCCHESI, JOHN W. BEVAN, and RICHARD D. SUENRAM

- F35 – *SLIT JET INFRARED ABSORPTION SPECTROSCOPY OF C₂H₂ – HCl COMPLEXES*
P. CARCABAL, M. CHEVALIER, M. BROQUIER,
 and A. PICARD-BERSELLINI
- F36 – *THE ELECTRONIC STATES OF THE FeH RADICAL : A PROGRESS REPORT*
CATHERINE WILSON, DANIEL F. HULLAH, RICHARD F. BARROW, and
 JOHN M. BROWN
- F37 – *FOURIER TRANSFORM EMISSION SPECTRUM OF THE ELECTRONIC C⁸II - X³II TRANSITION OF THE SiC RADICAL*
R. CIREASA, D. COSSART, and M. VERVLOET
- F38 – *A CONTINUED FRACTION EXPANSION OF THE BORN-OPPENHEIMER POTENTIAL ENERGY FUNCTION FOR DIATOMIC MOLECULES*
 M. MOLSKI
- F39 – *PREDICTION OF PREDISSOCIATION EFFECTS IN THE 0_v⁺(²P_{3/2}) STATE OF Rb₂ AND Cs₂, USING THE MAPPED FOURIER GRID HAMILTONIAN METHOD*
VIATCHESLAV KOKOULINE, OLIVIER DULIEU,
FRANÇOISE MASNOU-SEEUWS, and RONNIE KOSLOFF
- F40 – *SURFACE AND BULK DIFFUSION OF ATMOSPHERIC GASES ON ICE INVESTIGATED BY RESONANT INFRARED LASER DESORPTION / REMPI MASS SPECTROMETRY*
M. CORDONNIER, and J.-L. DESTOMBES

Invited Lectures G, Tuesday, September 7, 14:00

Chairman : P. JENSEN

- G1 – *NON LINEAR VIBRATIONAL SPECTROSCOPY OF MOLECULES IN SOLIDS AND AT SURFACES*
HENRI DUBOST
- G2 – *SINGLE, DOUBLE AND TRIPLE TRANSITIONS IN THE ROVIBRATIONAL SPECTRUM OF SOLID H₂, D₂ AND HD*
B. P. WINNEWISSER

Poster Session H, Tuesday, September 7, 16:00

- H1 – *DIRECT TWO PHOTON TRANSITIONS IN HIGH FREQUENCY ELECTRON PARAMAGNETIC RESONANCE DESCRIBED BY A 3-LEVEL DENSITY MATRIX FORMALISM*
W. LEO MEERTS, PAUL J.M. van KAN, and ETIENNE GOOVAERTS

- H2 - *HIGHLY-SENSITIVE DETECTION OF METHANE IN AIR BY DIODE-PUMPED, MID-INFRARED, DIFFERENCE-FREQUENCY GENERATION IN QUASI-PHASE-MATCHED LiNbO_3*
GUILHERME DE ANDRADE GARCIA, PIN CHEN, and LEO HOLLBERG
- H3 - *CONSTRUCTION OF A THREE-DIODE-LASER, TERAHERTZ, DIFFERENCE-FREQUENCY SYNTHESIZER AND ITS APPLICATIONS TOWARD SPECTROSCOPY OF AMMONIA IN THE ν_2 STATE AND WATER IN THE GROUND AND ν_2 STATES*
PIN CHEN, JOHN C. PEARSON, HERBERT M. PICKETT, SHUJI MATSUURA, and GEOFFREY A. BLAKE
- H4 - *THEORETICAL STUDY OF TWO-PHOTON ABOVE THRESHOLD DISSOCIATION AND RELATED PROCESSES IN ALKALI MOLECULAR IONS*
S. MAGNIER, M. PERSICO, N. RAHMAN, and M. AUBERT-FRECON
- H5 - *VIBRATIONAL RELAXATION AND HOT LUMINESCENCE OF SELF-TRAPPED EXCITONS IN ATOMIC CRYOCRYSTALS*
M. SELG, V. HIZHNYAKOV, M. KINK, R. KINK, R. LÖHMUS, and J. MAK-SIMOV
- H6 - *IONIC MOTIONS AND PHASE TRANSITIONS OF $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ STUDIED BY ^1H NMR*
SETSUKO SATO, AKIKO IDO, and HIROYUKI ISHIDA
- H7 - *UV LASER SPECTROSCOPY USING THE VELOCITY MODULATION TECHNIQUE : STUDY OF A $\text{SiCl}_4/\text{O}_2/\text{He}$ DISCHARGE AROUND 325 NM*
D. COLLET, B. PINCHEMEL, and T. R. HUET
- H8 - *UV LASER SPECTROSCOPY USING THE VELOCITY MODULATION TECHNIQUE : NEW HOT BANDS OF THE $B^2\Sigma_u^+ - X^2\Sigma_g^+$ SYSTEM OF N_2^+*
D. COLLET, and T. R. HUET
- H9 - *COMPUTATIONAL ANALYSIS OF WATER ABSORPTIONS AT NEAR INFRARED AND VISIBLE WAVELENGTHS*
D. BELMILOUD, O. L. POLYANSKY, and J. TENNYSON
- H10 - *SUPERSONIC SLIT NOZZLE PLASMAS: AN OVERVIEW*
H. LINNARTZ, J. P. MAIER, T. MOTYLEWSKI, D. PFLUGER, W. E. SINCLAIR, O. VAIZERT, and D. VERDES
- H11 - *THE ROTATIONAL SPECTRUM OF IODINE DIOXIDE, OIO*
CHARLES E. MILLER, and EDWARD A. COHEN
- H12 - *SPECTROSCOPY OF CHLOROSYL FLUORIDE, FCIO*
HOLGER S. P. MÜLLER, and EDWARD A. COHEN
- H13 - *ANALYSIS OF THE EMISSION OF THE HS_2 RADICAL FROM THE \tilde{A}^2A' STATE DETECTED BY NIR FOURIER TRANSFORM SPECTROSCOPY*
S. H. ASHWORTH, and E. H. FINK

- H14 – HIGH-RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF $^{14}\text{N}_2$ MOLECULE: FIRST OBSERVATION OF THE $\Delta v = 1$ SEQUENCES OF THE B-W SYSTEM. GLOBAL ROTATIONAL ANALYSIS OF THE B' $^3\Sigma_u^-$, W $^3\Delta_u$, B $^3\Pi_g$, AND A $^3\Sigma_u^+$ STATES
A. FAYE, Q. KOU, R. FARRENQ, and G. GUELACHVILI
- H15 – DETECTION OF FPO BY HIGH-RESOLUTION INFRARED SPECTROSCOPY
PETER PAPLEWSKI, HANS BÜRGER, and HELMUT BECKERS
- H16 – HIGH-RESOLUTION IR SPECTRUM OF SCF_2 FROM 1000 TO 1400 cm^{-1} : THE $\nu_1/\nu_3 + 2\nu_5/\nu_2 + \nu_3$ AND $\nu_4/\nu_2 + \nu_5$ INTERACTING STATES
JEAN-MARIE FLAUD, WOLFGANG JERZEMBECK, and HANS BÜRGER
- H17 – HIGH-RESOLUTION FTIR SPECTROSCOPY OF VINYL CHLORIDE IN THE REGION OF THE FUNDAMENTAL BANDS ν_{10} AND ν_{11}
A. DE LORENZI, S. GIORGIANNI, and R. BINI
- H18 – PRECISION FREQUENCY MEASUREMENTS OF NIR SPECTRAL LINES BY DIODE LASER SPECTROMETRY
M. THOMPSON, T.D. BEVIS, and J.G. BAKER
- H19 – HIGH RESOLUTION DIODE LASER SPECTROSCOPY OF THE NIR BANDS OF PROPYNE IN THE 12730 – 12790 cm^{-1} RANGE
T.D. BEVIS, and J.G. BAKER
- H20 – THE HIGH RESOLUTION FAR-INFRARED SPECTRUM OF VINYLAMINE
DON McNAUGHTON, and COREY EVANS
- H21 – THE PERPENDICULAR FUNDAMENTAL ν_5 OF CHLOROFORM $^{12}\text{CH}^{35}\text{Cl}_3$: HIGH RESOLUTION INFRARED STUDY OF THE ν_5 BAND TOGETHER WITH THE MILLIMETER-WAVE ROTATIONAL SPECTRUM
J. PIETILÄ, V.-M. HORNEMAN, R. ANTILA, B. LEMOINE, F. RAYNAUD, and J.-M. COLMONT
- H22a – ABSOLUTE LINE INTENSITIES AND BROADENINGS FOR THE 3-0 BAND OF $^{12}\text{C}^{16}\text{O}$
NATHALIE PICQUÉ, GUY GUELACHVILI, VICTOR DANA, and JEAN-YVES MANDIN
- H22b – HCN/HNC BETWEEN 2 AND 5 μm : FOURIER TRANSFORM EMISSION SPECTRA OF ASTROPHYSICAL INTEREST
NATHALIE PICQUÉ, and GUY GUELACHVILI
- H23 – LINESHAPE STUDY OF MILLIMETER TRANSITIONS OF CO AND O_3 PERTURBED BY N_2 AND O_2
J.-M. COLMONT, D. PRIEM, F. ROHART, G. WLODARCZAK, J.-P. BOUANICH, and R.R. GAMACHE

- H24 - *LINE INTENSITIES AND PRESSURE BROADENING OF ALL OZONE FUNDAMENTALS*
GEORG WAGNER, MANFRED BIRK, and JEAN-MARIE FLAUD
- H25 - *SPEED-DEPENDENT BROADENING AND LINE MIXING IN CH₄ PERTURBED BY AR AND N₂ FROM MULTISPECTRUM FITS*
A. S. PINE, and T. GABARD
- H26 - *POSITIONS AND INTENSITIES OF AMMONIA HOT BANDS IN THE 5 TO 8 μ m REGION AND IN THE 4 μ m REGION*
C. COTTAZ, I. KLEINER, G. TARRAGO, and L. R. BROWN
- H27 - *A NEW MULTIPLIER TERAHERTZ SPECTROMETER*
U. FUCHS, F. MAIWALD, F. LEWEN, and G. WINNEWISSER
- H28 - *HIGH RESOLUTION ANALYSIS OF THE A² Π -X² Σ ⁺ SYSTEM OF MgCl*
C. FELLOWS, M. VERVLOET, and R. F. GUTTERRES
- H29 - *QUANTUM DYNAMICS OF BENDING VIBRATIONS OF THE CH CHROMOPHORE IN SYMMETRIC AND ASYMMETRIC METHANE ISOTOPOMERS*
R. MARQUARDT, M. QUACK, and I. THANOPULOS
- H30 - *MODE SELECTIVE STEREOMUTATION IN HYDROGEN PEROXIDE: 6D TUNNELING AND WAVE PACKET DYNAMICS*
BENJAMIN FEHRENSSEN, DAVID LUCKHAUS, and MARTIN QUACK
- H31 - *MICROSOLVATION OF FUNDAMENTAL CARBOCATIONS*
O. DOPFER, R. V. OLKHOV, and S. A. NIZKORODOV
- H32 - *JET-FTIR SPECTROSCOPY OF MEDIUM STRENGTH HYDROGEN BONDING COMPLEXES OF B:H(D)X (B=DIMETHYLETHER, X=CL, F)*
P. ASSELIN, P. SOULARD, M.E. ALIKHANI, and J.P. PERCHARD
- H33 - *COULOMB EXPLOSION IMAGING AND THE CH₂⁺ MOLECULE*
GERALD OSMANN, P. R. BUNKER, W. P. KRAEMER, and PER JENSEN
- H34 - *ELECTRONIC STRUCTURE INCLUDING SPIN-ORBIT EFFECTS FOR THE DIMERS OF RUBIDIUM AND CESIUM*
S. ROUSSEAU, A.R. ALLOUCHE, and M. AUBERT-FRECON
- H35 - *AN IMPROVED POTENTIAL ENERGY CURVE FOR THE GROUND STATE OF NaK*
I. RUSSIER-ANTOINE, A.J. ROSS, M. AUBERT-FRECON,
and P. CROZET
- H36 - *A NEW PREDISSOCIATION OF N₂⁺ REVEALED BY FAST ION BEAM LASER SPECTROSCOPY AND ATTRIBUTED TO THE A² Π_u STATE*
M. LARZILLIÈRE, C. FRIGON, M. PARADIS, and C. J. DELISLE
- H37 - *COHERENT CONTROL OF ROTATIONAL WAVE PACKETS IN LINEAR MOLECULES*
E. HERTZ, O. FAUCHER, B. LAVOREL, F. DALLA VIA, and R. CHAUX

- H38 – *MANIFESTATION OF THE STRONG QUADRUPLE LIGHT MOLECULE INTERACTION IN THE SURFACE ENHANCED OPTICAL EFFECTS*
A.M. POLUBOTKO
- H39 – *VIBRATIONAL SPECTRA OF C₆H₆, C₆D₆ AND OF C₆D₅H*
E. CANÉ, A. TROMBETTI, A. MIANI, and M. BECUCCI
- H40 – *INFIA - PROGRAM FOR ROTATIONAL ANALYSIS OF LINEAR MOLECULE SPECTRA*
ROBERT BROTHERUS

Invited Lectures I, Wednesday, September 8, 9:00

Chairman : P. R. BUNKER

- I1 – *THE PAST, PRESENT AND FUTURE OF QUANTUM CHEMISTRY*
T. DANIEL CRAWFORD, STEVEN S. WESOLOWSKI,
EDWARD F. VALEEV, ROLLIN A. KING, MATTHEW L. LEININGER,
and HENRY F. SCHAEFER III
- I2 – *AB INITIO STUDIES ON VIBRATION-ROTATION SPECTRA OF REACTIVE MOLECULES*
W. THIEL

Poster Session J, Wednesday, September 8, 11:00

- J1 – *AB INITIO CALCULATIONS FOR INTENSITIES OF TEN ROTATION VIBRATION BANDS OF HYDROGEN SULPHIDE*
THIBAUD COURS, PAVEL ROSMUS, and VLADIMIR G. TYUTEREV
- J2 – *AB INITIO POTENTIAL ENERGY SURFACE AND INTERNAL TORSIONAL-WAGGING STATES OF HYDRAZINE*
W. LODYGA, and J. MAKAREWICZ
- J3 – *INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN THE CHIRAL MOLECULE CF₃CHF: EXPERIMENT AND AB INITIO THEORY*
JÖRG POCHERT, MARTIN QUACK, and MARTIN WILLEKE
- J4 – *SPECTROSCOPIC AND AB INITIO INVESTIGATION OF THE ν_{OH} OVERTONE EXCITATION IN TRANS-FORMIC ACID*
D. HURTMANS, F. HERREGODTS, M. HERMAN, J. LIÉVIN, A. CAMPARGUE, A. GARNACHE, and A. A. KACHANOV
- J5 – *AB INITIO CALCULATIONS ON THE QUASILINEAR MOLECULES CICNO AND BrCNO*
JACEK KOPUT

- J6 - MICROWAVE SPECTRUM, CONFORMATION, BARRIER TO INTERNAL ROTATION ^{14}N QUADRUPOLE COUPLING CONSTANTS, DIPOLE MOMENT AND QUANTUM CHEMICAL CALCULATIONS FOR METHYL CARBAMATE
K.-M. MARSTOKK, and HARALD MØLLENDAL
- J7 - MICROWAVE SPECTRUM OF DEUTERATED METHANE AND WATER COMPLEX
YOSHIYUKI KAWASHIMA
- J8 - TIME RESOLVED MMW/MMW DOUBLE RESONANCE SPECTROSCOPY ON METHYL FLUORIDE: OBSERVATION OF A K-CHANGING COLLISION PROCESS
MARKUS MENGEL, CHRISTOPHER D. BALL, and FRANK C. DE LUCIA
- J9 - MICROWAVE AND MILLIMETERWAVE SPECTRUM OF ACETIC ACID
I. KLEINER, B. MATÉ, E. KARYAKIN, R. D. SUENRAM, G. T. FRASER, J. T. HOUGEN, L. MARGULÈS, J. DEMAISON, G. WLODARCZAK, J. COSLÉOU, V. V. ILYUSHYN, E. A. ALEKSEEV, and S. F. DYUBKO
- J10 - THE ROTATIONAL SPECTRUM OF NF_3 IN THE VIBRATIONAL STATE $\nu_4=1$
ULF WÖTZEL, HAUKE HARDER, HEINRICH MÄDER, LAURENT MARGULÈS, JEAN COSLÉOU, JEAN DEMAISON, and LUCIANO FUSINA
- J11 - THE MICROWAVE SPECTRA OF BENZOTHAZOLE AND 2-METHYLBENZOTHAZOLE
A. WELZEL, and W. STAHL
- J12 - HIGH RESOLUTION SPECTRUM AND ROVIBRATIONAL ANALYSIS OF THE ν_2 / ν_5 DYAD OF D_3SiF NEAR 700 cm^{-1}
M. BADAoui, N. BEN SARI-ZIZI, G. GRANER, E.B. MKADMI, H. BÜRGER, and P. PRACNA
- J13 - HIGH-RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY AND ANALYSIS OF THE ν_3 FUNDAMENTAL BAND OF P_4
V. BOUDON, G. PIERRE, E.B. MKADMI, and H. BÜRGER
- J14 - FOURIER TRANSFORM HIGH RESOLUTION STUDY OF BaI MOLECULE: THE FIRST SEVEN LOW-LYING ELECTRONIC STATES
R. F. GUTTERRES, J. VERGÈS, and C. AMIOT
- J15 - EXTENDED ASSIGNMENTS, VIBRATIONAL COUPLING, AND MODELING FOR THE C-O STRETCH BAND OF CH_3OH
R. M. LEES, and LI-HONG XU
- J16 - THE BANDS OF CH_4 BETWEEN 5900 cm^{-1} AND 6200 cm^{-1} : $2\nu_3$ AND $2\nu_2 + \nu_3$
O. ROBERT, J.-C. HILICO, M. LOETE, and L.R. BROWN
- J17 - A COMBINED ANALYSIS OF THE ν_9 BAND AND THE FAR-INFRARED TORSIONAL SPECTRA OF ETHANE
N. MOAZZEN-AHMADI, J. SCHRODERUS, and A.R.W. MCKELLAR

- J18 – DIODE LASER SPECTROSCOPY OF $\text{CH}_2^{81}\text{BrF}$ IN THE ν_4 REGION
A. BALDACCI, and P. STOPPA
- J19 – THE MYSTERY OF A BAND VANISHING UPON ISOTOPIC SUBSTITUTION. THE CASE OF THE $\nu_3 = 1$ STATE OF FCLO_3
KAMIL SARKA, and GEORGES GRANER
- J20 – ROTATIONAL TRANSITIONS IN HOT EMISSION HDO SPECTRUM IN THE $400\text{-}850\text{ cm}^{-1}$ REGION AND HIGH- J , K_a ENERGY LEVELS OF THE (000) AND (010) STATES
SEMEN MIKHAILENKO, VLADIMIR G. TYUTEREV,
and GEORG Ch. MELLAU
- J21 – EXPERIMENTAL AND THEORETICAL STUDY OF LINE MIXING IN METHANE SPECTRA. THE Q BRANCH OF THE RAMAN ν_1 BAND PERTURBED BY He AND Ar
D. PIERONI, J.-M. HARTMANN, F. CHAUSSARD, X. MICHAUT,
T. GABARD, R. SAINT-LOUP, H. BERGER, and J.-P. CHAMPION
- J22 – MEASUREMENT OF PRESSURE SHIFTING OF ONE METHANE LINE IN THE $1.6\text{ }\mu\text{m}$ REGION
V. ZENINARI, D. COURTOIS, and Yu. N. PONOMAREV
- J23 – LINE PARAMETERS OF $^{12}\text{C}^{16}\text{O}_2$ IN THE $1.2\text{-}1.3\text{ }\mu\text{m}$ REGION
J.-L. TEFFO, C. CLAVEAU, Q. KOU, G. GUELACHVILI, A. UBELMANN,
V.I. PEREVALOV, and S.A. TASHKUN
- J24 – PRESSURE-SHIFT AND PRESSURE-BROADENING IN THE $\nu_1 + 3\nu_3$ BAND OF ACETYLENE IN THE NIR RANGE
F. HERREGODTS, D. HURTMANS, M. HEPP, J. VANDER AUWERA, and
M. HERMAN
- J25 – THE VIBRATIONAL ENERGY PATTERN IN ACETYLENE ISOTOPOMERS
M. I. EL IDRISI, J. LIÉVIN, M. HERMAN, and A. CAMPARGUE
- J26 – COLOGNE SIDEBAND SPECTROMETER FOR THz APPLICATIONS (COSSTA)
R. GENDRIESCH, F. LEWEN, J. STUTZKI, and G. WINNEWISSER
- J27 – HIGH RESOLUTION ANALYSIS OF THE $K_a = 0 \leftarrow 1$ SUBBANDS OF THE FUNDAMENTALS ν_3 AND ν_6 OF $(\text{HF})_2$
HANS HOLLENSTEIN, and MARTIN QUACK
- J28 – CURVILINEAR INTERNAL VALENCE COORDINATE HAMILTONIAN FOR AMMONIA
JANNE PESONEN, and LAURI HALONEN
- J29 – A HINDERED-ROTOR MODEL HAMILTONIAN FOR HCN/CNH
DOMINIQUE SUGNY, and MARC JOYEUX

- J30 – HIGH RESOLUTION SPECTROSCOPY OF THE $A^1\Sigma^+ - X^1\Sigma^+$ SYSTEM OF LiH
N. BOULOUPA, L. CABARET, P. CACCIANI, P. CAMUS, R. VETTER, and A. YIANOPOULOU
- J31 – ELECTRONIC GROUND AND EXCITED STATE SPECTROSCOPY OF C_6H AND C_6D
H. LINNARTZ, T. MOTYLEWSKI, O. VAIZERT, J. P. MAIER, A. J. AP-
PONI, M. C. MCCARTHY, P. THADDEUS, and C. A. GOTTLIEB
- J32 – HIGH RESOLUTION INFRARED SPECTROSCOPY OF IONIC COM-
PLEXES
H. LINNARTZ, D. VERDES, and J.P. MAIER
- J33 – THE STABLE CONFIGURATIONS OF $(H_2O)_n(HF)_m$ COMPLEXES IN
THE ATMOSPHERE
N.A. ZVEREVA, Yu.N. PONOMAREV, and Sh.Sh. NABIEV
- J34 – ABSORPTION SPECTROSCOPY OF THE GeH_2 RADICAL
NEAR 585 nm
A. CAMPARGUE, and R. ESCRIBANO
- J35 – STATE-TO-STATE ENERGY TRANSFER IN ELECTRONICALLY EX-
CITED NH_2 , OBSERVED WITH TIME RESOLVED FOURIER TRANS-
FORM EMISSION SPECTROSCOPY IN THE VISIBLE
RALF WILHELM, and JÖRG LINDNER
- J36 – HIGH RESOLUTION RAMAN SPECTRUM OF $^{12}C_2D_2$: THE ν_2 FUN-
DAMENTAL AND ASSOCIATED HOT BANDS
D. BERMEJO, J. L. DOMÈNECH, L. FUSINA, and G. DI LONARDO
- J37 – LOOSELY BOUND STATES OF A TRIATOMIC MOLECULE, INFLU-
ENCE OF THE LONG RANGE ELECTROSTATIC INTERACTIONS ON
THE DENSITY OF LEVELS
SYLVAIN HEILLIETTE, RÉMY JOST, and ANTOINE DELON
- J38 – ROTATIONAL SPECTRA, HYPERFINE STRUCTURE, AND NUCLEAR
MAGNETIC SHIELDING TENSORS OF $^{33}SO_2$ AND $SO^{17}O$
HOLGER S. P. MÜLLER, GISBERT WINNEWISSER,
EDWARD A. COHEN, MARTIN SCHÄFER,
BETHANY BRUPBACHER-GATEHOUSE, and ALFRED BAUDER
- J39 – ANALYTIC METHOD AND SOFTWARE FOR ONE-DIMENSIONAL
QUANTUM-MECHANICAL CALCULATIONS
M. SELG
- J40 – GENERAL CONCEPTS OF THE 1999 VERSION OF THE HILRAPSS99-
HIGH/LOW RESOLUTION ANALYSIS/PREDICTION OF SPECTRA
SOFTWARE
G. Ch. MELLAU, and M. WINNEWISSER

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

Chairman : J.-M. FLAUD

- K1 – *HIGH-RESOLUTION LABORATORY SPECTROSCOPY FOR REMOTE-SENSING OF ATMOSPHERIC TRACE GASES*
JOHANNES ORPHAL
- K2 – *ELECTRONIC SPECTRA OF CARBON CHAINS IN THE GAS PHASE AND THEIR RELATION TO THE DIFFUSE INTERSTELLAR BANDS*
J. P. MAIER

Poster Session L, Thursday, September 9, 11:00

- L1 – *IN SITU MONITORING OF STRATOSPHERIC CH₄ AND H₂O USING TELECOMMUNICATION DIODE LASERS*
G. DURRY, and G. MEGIE
- L2 – *TEMPERATURE DEPENDENT REFERENCE SPECTRA OF O₃, NO₂, AND OTHER ATMOSPHERIC TRACE GASES MEASURED WITH THE SCIAMACHY SATELLITE SPECTROMETER*
K. BOGUMIL, J. ORPHAL, and J. P. BURROWS
- L3 – *REMOTE-SENSING OF ATMOSPHERIC TRACE GASES BY MEANS OF GROUND-BASED HIGH-RESOLUTION SPECTROSCOPY*
T. HOMANN, A. VOGEL, J. ORPHAL, and J. P. BURROWS
- L4 – *TRACE GAS DETECTION WITH SEMICONDUCTOR LASERS*
E. NORMAND, G. DUXBURY, N. LANGFORD, C. IRONSIDE, C. FARMER, I. HOWIESON, T. GARDINER, N. SWANN, and P. WOODS
- L5 – *FTIR REMOTE SENSING OF ATMOSPHERIC COMPOUNDS : APPLICATION TO GLOBAL CHANGE*
GABRIEL J. VÁZQUEZ
- L6 – *THE 4¹Π AND 5¹Π STATES OF NaK: THE EXPERIMENTAL AND THEORETICAL STUDY*
P. KOWALCZYK, W. JASTRZĘBSKI, A. PASHOV, S. MAGNIER, and M. AUBERT-FRÉCON
- L7 – *THE ROTATIONAL SPECTRA OF IO AND BrO*
 CHARLES E. MILLER, EDWARD A. COHEN, and HOLGER S. P. MÜLLER
- L8 – *VIBRATIONALLY EXCITED HCN, HC₃N, AND HC₅N TOWARD CRL 618*
SVEN THORWIRTH, GISBERT WINNEWISSER, FRIEDRICH WYROWSKI, and PETER SCHILKE

- L9 - *THE ROTATIONAL SPECTRUM OF SO₂F₂. THE FIRST DETERMINATION OF ALL SIX QUARTIC CENTRIFUGAL DISTORTION CONSTANTS FROM THE SPECTRA OF AN ASYMMETRIC ROTOR*
JEAN DEMAISON, KAMIL SARKA, LAURENT MARGULÉS, ILONA MERKE, and NILS HEINEKING
- L10 - *PSEUDOROTATION IN 1,3-DITHIOLANE: A MICROWAVE STUDY*
J. C. LÓPEZ, S. BLANCO, A. LESARRI, J. L. ALONSO, J. LAANE, and J. R. VILLAREAL
- L11 - *SUBMILLIMETREWAVE SPECTRUM OF FLUOROACETYLENE (H-C≡C-F) IN VIBRATIONALLY EXCITED STATES*
A. HUCKAUF, and A. GUARNIERI
- L12 - *HIGH RESOLUTION ANALYSIS OF THE ν_1 AND ν_3 BANDS OF THE ¹⁷O¹⁷O¹⁶O AND ¹⁷O¹⁶O¹⁷O ISOTOPIC SPECIES OF OZONE IN THE 10 μ m REGION*
A. PERRIN, J.-M. FLAUD, A. VALENTIN, and C. CAMY-PEYRET
- L13 - *HIGH RESOLUTION INFRARED SPECTRUM OF THE RING-PUCKERING BAND, ν_{10} , OF DIBORANE*
W. J. LAFFERTY, J.-M. FLAUD, R. L. SAMS, T. A. BLAKE, and S. W. SHARPE
- L14 - *RECENT PROGRESS IN LASER-INDUCED THERMAL ANISOTROPY PATTERNS AND APPLICATIONS*
X. CHEN, H. BERGER, B. LAVOREL, and R. CHAUX
- L15 - *ABSOLUTE LINE INTENSITIES IN THE 2 μ m REGION OF ¹⁴N₂¹⁶O*
L. DAUMONT, J.-L. TEFFO, J. VANDER AUWERA, V.I. PEREVALOV, and S.A. TASHKUN
- L16 - *ABSOLUTE LINE INTENSITIES MEASUREMENTS IN THE $\nu_4 + \nu_5$ BAND OF ¹²C₂H₂: STUDY OF FORBIDDEN TRANSITIONS AND HERMAN-WALLIS DEPENDENCIES*
J. VANDER AUWERA, and Y. EL YOUSOUFI
- L17 - *THE HOT BAND OF SILANE BETWEEN 2120 AND 2270 cm⁻¹*
M. TERKI-HASSAÏNE, N. PICQUÉ, G. GUELACHVILI, G. PIERRE, and A. BABA-AHMED
- L18 - *HIGH-RESOLUTION INFRARED STUDY OF cis-1,2-DIFLUOROETHYLENE NEAR 1020 cm⁻¹*
R. VISINONI, S. GIORGIANNI, and S. GHERSETTI
- L19 - *MEASUREMENTS OF OZONE ISOTOPOMER ABUNDANCES USING HIGH RESOLUTION FOURIER TRANSFORM FAR INFRARED SPECTROSCOPY*
RENÉ WUGT LARSEN, NIELS WESSEL LARSEN, FLEMMING M. NICOLAISEN, GEORG OLE SØRENSEN, and JON ARE BEUKES

- L20 – AIR-BROADENING AND SELF-BROADENING OF PURE ROTATIONAL O_3 LINES AND THEIR TEMPERATURE DEPENDENCE
RENÉ WUGT LARSEN, FLEMMING M. NICOLAISEN, and GEORG OLE SØRENSEN
- L21 – THE IMPORTANCE OF NO+O COLLISIONAL RELAXATION TO THERMOSPHERIC COOLING AND REMOTE SENSING OF NO
B. FUNKE, G. STILLER, T. V. CLARMANN, M. HÖPFNER, and M. LÓPEZ-PUERTAS
- L22 – PRECISE MEASUREMENT OF TEMPERATURE DEPENDENT PRESSURE EFFECTS
T. DRASCHER, U. FUCHS, T. GIESEN, R. SCHIEDER, and G. WINNEWISSER
- L23 – COLLISION LINE NARROWING AND MIXING FOR H_2O DOUBLETS NEARBY 2000 cm^{-1}
SINITSA L.N., KOCHANOV V.P., SAVELIEV V.N., Ch. CLAVEAU, and A. VALENTIN
- L24 – N_2 BROADENING IN R BRANCH OF THE (010)-(000) BAND OF H_2O
L.N. SINITSA, V.P. KOCHANOV, V.N. SAVELIEV, A. VALENTIN, and Ch. CLAVEAU
- L25 – THE HIGH RESOLUTION INFRARED SPECTRUM OF DIMETHYLETHER
PIERRE CARCABAL, MICHELE CHEVALIER, MICHEL BROQUIER, LAURENT H. COUDERT, M. HERMAN, and MARTIN HEPP
- L26 – ON ISOTOPE EFFECT IN THE $XH_2 - XHD$ MOLECULES WITH AN ARBITRARY VALUE OF EQUILIBRIUM INTERBOND ANGLE
O.N. ULENIKOV, S.N. YURCHENKO, V.V. MELNIKOV, and E.S. SINITSIN
- L27 – ROVIBRATIONAL STRUCTURE USING QUANTUM-CLASSICAL CORRESPONDENCE: HOW PROMINENT IS THE INFLUENCE OF THE INTRAMOLECULAR POTENTIAL ON THE QUALITATIVE FEATURES OF THE SYSTEM OF ENERGY LEVELS ?
C. VAN-HECKE, D. SADOVSKIÍ, and B. ZHILINSKIÍ
- L28 – ALTERNATIVE CHOICES OF QUANTUM NUMBERS. DEFECTS OF LABELING SCHEMES AND CLASSICAL MONODROMY
B. ZHILINSKII, and D. SADOVSKII
- L29 – HIGH RESOLUTION ELECTRONIC SPECTRA OF CARBON CHAIN RADICAL CATIONS BY FREQUENCY MODULATION ABSORPTION SPECTROSCOPY
WAYNE E. SINCLAIR, DAVID PFLUGER, HAROLD LINNARTZ, and JOHN P. MAIER

- L30 - *ROTATIONALLY RESOLVED ELECTRONIC ABSORPTION SPECTRA OF CYANOPOLYACETYLENE CATIONS*
WAYNE E. SINCLAIR, DAVID PFLUGER, HAROLD LINNARTZ,
and JOHN P. MAIER
- L31 - *SPECTROSCOPIC AND THEORETICAL CHARACTERIZATION OF LINEAR CENTROSYMMETRIC $N\equiv N\cdots H^+\cdots N\equiv N$*
D. VERDES, H. LINNARTZ, J. P. MAIER, P. BOTSCHWINA, R. OSWALD,
P. ROSMUS, and P. KNOWLES
- L32 - *AXIAL AND EQUATORIAL HYDROGEN BONDS*
J. C. LÓPEZ, M. E. SANZ, S. ANTOLÍNEZ, S. BLANCO, A. LESARRI, and
J. L. ALONSO
- L33 - *SYSTEMATIC VIBRATIONAL SHIFTS OF CARBON DIOXIDE MONOMERS AND DIMERS TRAPPED IN VARIOUS MATRICES*
A. A. VIGASIN, L. SCHRIVER-MAZZUOLI, and A. SCHRIVER
- L34 - *INFRARED SPECTRA OF CO-H₂O AND CO-D₂O CLUSTERS IN Ar MATRIX*
HISASHI ABE, and KOICHI M. T. YAMADA
- L35 - *CONSTRUCTING THE PERFECT GROUND STATE POTENTIAL FOR WATER*
SOPHIE KAIN, OLEG POLYANSKY, and JONATHAN TENNYSON
- L36 - *HIGH RESOLUTION MICROWAVE SPECTROSCOPY OF CHIRAL MOLECULES*
ADRIAN K. KING, and BRIAN J. HOWARD
- L37 - *ROTATIONAL ANALYSIS OF THE $[O_2(^1\Delta_g)_{v=0}]_2 \leftarrow [O_2(^3\Sigma_g^-)_{v=0}]_2$ TRANSITION OF THE O₂ DIMER NEAR 632.6 nm*
L. BIENNIER, D. ROMANINI, A. KACHANOV, A. CAMPARGUE,
B. BUSSERY-HONVAULT, V. VEYRET, A. J. BOUVIER, S. CHURASSY,
and R. BACIS
- L38 - *INVESTIGATION OF QUALITATIVE PHENOMENA IN ROTATIONAL DYNAMICS OF MOLECULES. MICROSCOPIC APPROACH TO THE PROBLEM*
SERGEI V. PETROV, and SERGEI E. LOKSHTANOV
- L39 - *ROVIBRATIONAL ENERGY TRANSFER IN METHANE STUDIED BY LASER-INDUCED FLUORESCENCE AND TIME RESOLVED IR-IR DOUBLE RESONANCE*
F. MENARD-BOURCIN, L. DOYENNETTE, J. MENARD, and C. BOURSIER
- L40 - *THE HIGH-RESOLUTION INFRARED SPECTRUM OF 1,2,4-TRIAZINE VAPOR BETWEEN 550 AND 1700 cm⁻¹*
D. THASTUMBACH, F. HEGELUND, J. A. BEUKES, F. M. NICOLAISEN,
and M. H. PALMER

Poster Session M, Thursday, September 9, 20:00

- M1 – *TIME RESOLVED DOPPLER-LIMITTED FOURIER TRANSFORM EMISSION SPECTRA OF $^{14}\text{N}_2$*
A. FAYE, N. PICQUÉ, Q. KOU, R. FARRENQ., and G. GUELACHVILI
- M2 – *NUCLEAR SPIN CONVERSION IN CH_3F INDUCED BY ALTERNATING ELECTRIC FIELD*
J. COSLÉOU, F. HERLEMONT, M. KHELKHAL, J. LEGRAND,
and P.L. CHAPOVSKY
- M3 – *NEW SEARCH FOR PARITY VIOLATING EFFECTS IN CHIRAL MOLECULES*
Ch. CHARDONNET, Ch. DAUSSY, T. MARREL, M. ZISKIND, A. AMY-KLEIN, and Ch. BORDÉ
- M4 – *FIRST OBSERVATION OF MATTER WAVE INTERFERENCE ON A K_2 MOLECULAR BEAM*
M. FRANK, C. LISDAT, H. KNÖCKEL, and E. TIEMANN
- M5 – *QUANTUM BEAT MEASUREMENT OF THE MAJORANA EFFECT IN A MOLECULE*
HUBERTUS RING, ROBERT T. CARTER, and J. ROBERT HUBER
- M6 – *NUCLEAR QUADRUPOLE EFFECTS ON THE PRESSURE BROADENING OF CH_3I IN THE $\nu_6=1$ EXCITED STATE*
G. BUFFA, A. DI LIETO, P. MINGUZZI, O. TARRINI, and M. TONELLI
- M7 – *ROTATIONAL SPECTRA OF ^{13}C AND ^{15}N ISOTOPOMERS OF CYANOACETYLENE (HC_3N) IN THE GROUND AND VIBRATIONALLY EXCITED STATES*
SVEN THORWIRTH, HOLGER S. P. MÜLLER,
and GISBERT WINNEWISSER
- M8 – *TERAHERTZ SPECTROSCOPY OF THE DIATOMIC MOLECULES SH, PH, AND NO*
E. KLISCH, S. P. BELOV, and G. WINNEWISSER
- M9 – *MICROWAVE SPECTRUM, CONFORMATIONAL EQUILIBRIUM AND QUANTUM CHEMICAL CALCULATIONS OF URETHANE (ETHYL CARBAMATE)*
K.-M. MARSTOKK, and HARALD MØLLENDAL
- M10 – *MILLIMETER-WAVE SPECTROSCOPY OF PHOSPHA-ALKYNES: HC_3P AND NC_2P*
LUCA BIZZOCCHI, and CLAUDIO DEGLI ESPOSTI
- M11 – *HIGH RESOLUTION ANALYSIS OF THE $3\nu_3$ AND $2\nu_1 + \nu_3$ BANDS OF NITROGEN DIOXIDE BY FOURIER TRANSFORM SPECTROSCOPY*
T.M. STEPHEN, A. GOLDMAN, A. PERRIN, C.P. RINSLAND,
J.-M. FLAUD, and F. KELLER

- M12 - HIGH RESOLUTION ANALYSIS OF HDCl IN THE 10 μm REGION
A. PERRIN, J.-M. FLAUD, M. SMIRNOV, and M. LOCK
- M13 - INFRARED STUDY ON THE PAPE BAND ($\nu_6 + \nu_8$)⁰ AND THE HOT BANDS $\nu_6 + \nu_8 - \nu_8$ OF CD₃CN
S. ALANKO, R. ANTTILA, M. KOIVUSAARI, V.-M. HORNEMAN,
R. PASO, and V. ORRE
- M14 - STUDY OF THE GROUND AND LOWEST VIBRATIONAL STATES OF THE ¹³CH₃D MOLECULE
O.N. ULENIKOV, N.E. TYABAEVA, and E. BEKHTEREVA,
J. SCHRODERUS, S. ALANKO, and R. ANTTILA
- M15 - TUNNELING-ROTATION TRANSITION OF MALONALDEHYDE OBSERVED IN THE SUBMILLIMETER-WAVE REGION
ISAMU MORINO, KOICHI M.T. YAMADA, TAKESHI BABA, TAKEHIKO TANAKA, and KEIICHI TANAKA
- M16 - THE ν_1 AND ν_3 BAND OF ND₃
LUCIANO FUSINA, HANS HOLLENSTEIN, MARTIN QUACK,
and MARCEL SNELS
- M17 - MEASUREMENT OF NEAR-INFRARED AND VISIBLE ABSORPTION CROSS-SECTIONS OF WATER VAPOUR
D. A. NEWNHAM, R. G. WILLIAMS, and J. BALLARD
- M18 - INFRARED LASER SPECTROSCOPY OF THE ν_4 AND ν_6 FUNDAMENTALS OF *cis*-CHCl=CHF
P. STOPPA, A. PIETROPOLLI CHARMET, S. GIORGIANNI,
and S. GHERSETTI
- M19 - UPDATED ELECTRIC DIPOLE MOMENT FUNCTION FOR CARBON MONOXIDE
C. CHACKERIAN, JR., R. S. FREEDMAN, L. P. GIVER, R. KSHIRSAGAR,
and L. R. BROWN
- M20 - COLLISION INDUCED SPECTRA IN THE FUNDAMENTAL OF N₂ AND O₂
G. MOREAU, J. BOISSOLES, R. Le DOUCEN, C. BOULET, W.J. LAFERTY, R.H. TIPPING, and Q. MA
- M21 - INFLUENCE OF THE TRANSLATIONAL MODELLING ON THE FAR WING RAMAN SCATTERING SPECTRUM
L. BONAMY, and J. BULDYREVA
- M22 - INHOMOGENEOUS PROFILES FROM THE DOPPLER TO THE COLLISIONAL REGIME : ANALYSIS OF H₂ RAMAN SPECTRA WITH A UNIFIED MODEL
F. CHAUSSARD, X. MICHAUT, R. SAINT-LOUP, H. BERGER, P. JOUBERT, B. LANCE, J. BONAMY, and D. ROBERT

- M23 – *STUDY OF ROTATIONAL RELAXATION IN LINEAR MOLECULES WITH FEMTOSECOND RAMAN INDUCED POLARIZATION SPECTROSCOPY*
B. LAVOREL, O. FAUCHER, R. CHAUX, and M. MORGEN
- M24 – *QUANTUM INTERFERENCE IN A MOLECULAR IONIZATION CONTINUUM*
E. HERTZ, O. FAUCHER, B. LAVOREL, R. CHAUX, H. BERGER, and D. CHARALAMBIDIS
- M25 – *SPECTROSCOPIC AND THEORETICAL STUDY OF THE CH STRETCHING JET-COOLED SPECTRUM OF CYCLOPENTENE*
L. LESPADE, D. CAVAGNAT, S. RODIN-BERCION, and L. MANCERON
- M26 – *CLASSICAL INTERPRETATION OF THE ROTATIONAL STRUCTURE OF THE $\nu_6 = 1$ VIBRATIONAL LEVEL OF $M_o(CO)_6$*
G. DHONT, B. ZHILINSKII, D. SADOVSKII, and V. BOUDON
- M27 – *EFFECTIVE QUADRUPOLE COUPLING OPERATOR FOR QUASIDEGENERATE VIBRATIONAL STATES OF POLYATOMIC MOLECULES IN THEORY OF LINKED ORDERING SCHEMES OF ROVIBRATIONAL INTERACTIONS*
MIKHAILOV V.M., and SMIRNOV M.A
- M28 – *THE PHOTOELECTRON SPECTRUM OF NO_2 . AN AB-INITIO MRDCI STUDY*
C. GODOY, and GABRIEL J. VÁZQUEZ
- M29 – *THE $RbCs$ $X^1\Sigma^+$ ELECTRONIC GROUND STATE. NEW SPECTROSCOPIC STUDY*
C. FELLOWS, R. F. GUTTERRES, J. VERGÈS, C. AMIOT,
and A. P. C. CAMPOS
- M30 – *THE FOURIER TRANSFORM EMISSION SPECTRUM OF THE $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$ ELECTRONIC TRANSITION OF N_2O^+*
C. FELLOWS, and M. VERVLOET
- M31 – *HIGH RESOLUTION LASER SPECTROSCOPY OF THE $^{39}K^{85}Rb$ $1^1\Pi$ AND $2^1\Pi$ STATES*
S. KASAHARA, C. FUJIWARA, H. KATO, and M. BABA
- M32 – *DOPPLER-FREE HIGH RESOLUTION SPECTRAL ATLAS OF IODINE MOLECULE 15,000 TO 19,000 cm^{-1}*
H. KATÔ, S. KASAHARA, K. ISHIKAWA, M. MISONO, Y. KIMURA, J. O'REILLY, H. KUWANO, T. SHIMAMOTO, T. SHINANO, C. FUJIWARA, M. IKEUCHI, N. FUJITA, M. D. KABIR, M. USHINO, R. TAKAHASHI, Y. MATSUNOBU, and M. BABA
- M33 – *DEVELOPMENT OF JET-COOLED SUPERSONIC CARBON CLUSTER SOURCES*
G. FUCHS, T. GIESEN, U. BERNDT, R. BERGER, and G. WINNEWISSER

- M34 – *MOLECULAR EVOLUTION DESCRIPTION AND RESONANCE CALCULATING FOR ONE-DIMENSIONAL QUANTUM SYSTEMS*
T.Yu. MIKHAILOVA, and V.I. PUPYSHEV
- M35 – *GROUND-STATE POTENTIAL ENERGY SURFACE OF OZONE DETERMINED FROM RO-VIBRATIONAL SPECTRA*
VLADIMIR G. TYUTEREV, SERGEI TASHKUN, DAVID W. SCHWENKE, PER JENSEN, THIBAUD COURS, ALAIN BARBE, and MARCEL JACON
- M36 – *MULTI-CONFIGURATION LINEAR RESPONSE APPROACH TO THE CALCULATION OF PARITY VIOLATING POTENTIALS IN POLYATOMIC MOLECULES*
ROBERT BERGER, and MARTIN QUACK
- M37 – *HIGH RESOLUTION STIMULATED RAMAN SPECTRUM OF THE ν_2 Q-BRANCH REGION OF DIACETYLENE*
J. SANTOS, and D. BERMEJO
- M38 – *SOFTWARE FOR MEASURING LINE POSITIONS, STRENGTHS AND WIDTHS FROM HIGH RESOLUTION FOURIER TRANSFORM SPECTRA*
D. BARON, and N. LACOME
- M39 – *QUASI-LINE SPECTRA AND NH(ND) ISOMERISM IN METHYL DERIVATIVES OF ISOBACTERIOCHLORIN*
S. M. ARABEL, and K. N. SOLOVYOV
- M40 – *HYPERFINE STRUCTURES IN THE MICROWAVE SPECTRA OF STABLE SULFUR OXYFLUORIDES*
N. HEINEKING, and I. MERKE
- M41 – *THE TORSIONAL OVERTONE OF CH_3CF_3*
S.-X. WANG, J. SCHRODERUS, I. OZIER, N. MOAZZEN-AHMADI, and A. R. W. MCKELLAR
- M42 – *VIBRATION-TORSION-ROTATION ANALYSIS OF THE ν_{12} AND ν_{11} BANDS OF CH_3CF_3*
S.-X. WANG, J. SCHRODERUS, I. OZIER, N. MOAZZEN-AHMADI, and V.-M. HORNEMAN
- M43 – *INVESTIGATION OF VIBRONIC SPECTRA OF BISANTHENE AND HYPERICIN BY QUASI-LINE AND FINE-STRUCTURE FLUORESCENCE SPECTRA METHODS*
T. A. PAVICH
- M44 – *RELATIONS AMONG LINEAR VIBRATIONAL COORDINATES FOR DIFFERENT MOLECULAR ELECTRONIC STATES*
A.Ya. TSAUNE, and M.P. DYACHENKO
- M45 – *CALCULATION OF MOLECULAR PARAMETERS AND PREDICTION OF MICROWAVE TRANSITIONS OF CH_2DOD*
SUNIL G. BHAND, NIRANKAR N. MISHRA, and I. MUKHOPADHYAY

- M46 - *POWERFUL OPO/OPA SOURCES FOR IR LIDAR TECHNOLOGY*
I. YAKOVLEV, G. FREIDMAN, V. LOZHKAREV, and G. PASMNIK
- M47 - *PHOTODISSOCIATION DYNAMICS OF WATER MOLECULE AND ITS
 HYDROGEN-BONDED COMPLEXES IN THE FIRST ABSORPTION BAND*
 NATALIA A. ZVEREVA

Invited Lectures N, Friday, September 10, 9:00

Chairman : L. R. BROWN

- N1 - *SPECTRAL HEADLINES: THE (NON-)APPEARENCE OF
 SPECTROSCOPY IN THE MASS MEDIA*
S. MILLER
- N2 - *VIBRONIC COUPLING IN NH₂ AND CH₂, A PARTNERSHIP OF THE-
 ORY AND EXPERIMENT*
GEOFFREY DUXBURY

Poster Session O, Friday, September 10, 11:00

- O1 - *ENERGETIC, RADIATIVE AND MAGNETIC PROPERTIES OF THE
 $i^3\Pi_g^-$ AND $j^3\Delta_g^-$ STATES OF MOLECULAR HYDROGEN IN NONADIA-
 BATIC APPROXIMATION*
 E.A. PAZYUK, and S.O. ADAMSON
- O2 - *HYDROGEN BONDING, STRUCTURE AND DYNAMICS OF
 BENZONITRILE-WATER*
 S. MELANDRI, W. CAMINATI, P.G. FAVERO, and D. CONSALVO
- O3 - *MICROWAVE SPECTRUM, INTRAMOLECULAR HYDROGEN BOND-
 ING, CONFORMATIONAL PROPERTIES AND QUANTUM CHEMICAL
 CALCULATIONS FOR 3,3,3-TRIFLUOROPROPANOL*
 K.-M. MARSTOKK, and HARALD MØLLENDAL
- O4 - *MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF THIIRANE-
 ARGON AND THIIRANE-NEON VAN DER WAALS COMPLEXES*
D. PETITPREZ; S. KASSI, and G. WLODARCZAK
- O5 - *MICROWAVE SPECTRUM OF THE OPEN-SHELL VAN DER WAALS
 COMPLEX Ar-CIO₂*
MARTIN SCHÄFER, and ALFRED BAUDER
- O6 - *THE ν_6 AND ν_3 BANDS OF CD₃CN WITH STRONG CORIOLIS INTER-
 ACTION AND OTHER PERTURBATIONS*
S. ALANKO, R. ANTTILA, M. KOIVUSAARI, R. PASO, and J. PIETILÄ
- O7 - *THE N-N INFRARED BAND OF HYDRAZINE*
M. KREGLEWSKI, I. GULACZYK, and A. VALENTIN

- O8 - *MILLIMETER-WAVE STUDY OF CH₃SiD₃ IN THE ($v_6 = 0, 1, 2, 3$) AND ($v_{12} = 1$) STATES*
J. SCHRODERUS, I. OZIER, N. MOAZZEN-AHMADI, L. MARGULÈS, and J. COSLÉOU
- O9 - *THE ROTATIONAL SPECTRUM OF BiO IN ITS X₁²Π_{1/2} AND X₂²Π_{3/2} ELECTRONIC STATES*
EDWARD A. COHEN, DAMIAN M. GOODRIDGE,
and KENTAROU KAWAGUCHI
- O10 - *ANALYSIS OF THE ν₂ FUNDAMENTAL OF D₂CO WITH FERMI-TYPE INTERACTION ν₂/2ν₄*
JARMO LOHILATHI, SEPPO ALANKO, and MATTI KOIVUSAARI
- O11 - *THE MICROWAVE AND MM-WAVE SPECTRUM OF THE GROUND AND ONE TORSIONAL EXCITED STATE OF ACETONE*
P. GRONER, S. ALBERT, E. HERBST, F. C. DE LUCIA, and F. J. LOVAS
- O12 - *HIGH RESOLUTION ANALYSIS OF H₂CO IN THE 3.6 AND 4.3 μm REGION BY FOURIER TRANSFORM SPECTROSCOPY*
A. PERRIN, J.-M. FLAUD, A. VALENTIN, C. CAMY-PEYRET,
and L. R. BROWN
- O13 - *STUDY OF THE INFRARED ABSORPTION SPECTRUM OF SF₆ NEAR 950 cm⁻¹*
E. LOUBIGNAC, V. BOUDON, G. PIERRE, N. LACOME,
R. R. GAMACHE, F. HERLEMONT, M. KHELKHAL, and J. LEGRAND
- O14 - *STUDY OF THE FUNDAMENTAL BANDS OF ⁷⁰GeD₄ BY RAMAN AND INFRARED SPECTROSCOPY*
G. PIERRE, V. BOUDON, E.B. MKADMI, H. BÜRGER, D. BERMEJO,
and R. MARTÍNEZ
- O15 - *APPARENT PRESSURE SHIFT OF ROTATIONAL TRANSITIONS AS A CONSEQUENCE OF THE INTERNAL STRUCTURE OF LEVELS*
Š. URBAN, K. M. T. YAMADA, and G. WINNEWISSER
- O16 - *NEW FEATURES OF THE MOGADOC DATABASE (MOLECULAR GAS-PHASE DOCUMENTATION)*
JÜRGEN VOGT, WOLFGANG HUTTER, and NATALJA VOGT
- O17 - *COLLISIONAL COOLING: A ROUTE TO DETERMINING KEY PROPERTIES OF HYDROFLUOROCARBON VAPOURS RELEVANT TO GLOBAL WARMING*
K.M. WARD, G. DUXBURY, D. NEWNHAM, and J. BALLARD
- O18 - *TORSIONAL SPLITTINGS OF ⁷⁰Ge-DIGERMANE IN THE DEGENERATE VIBRATIONAL STATES*
C. DI LAURO, F. LATTANZI, H. BÜRGER, and E.B. MKADMI
- O19 - *DETECTION OF NO BY LASER MAGNETIC RESONANCE*
LARS MENZEL, WOLFGANG URBAN, and WILHELM BLOCH

- O20 – *THE IR-SPECTRUM OF DICYANOACETYLENE BETWEEN 1950 AND 3600 cm^{-1}*
F. WINTHER, M. SCHÖNHOF, A. HUCKAUF,
 and EL BACHIR MKADMI
- O21 – *COMPARISON BETWEEN QUANTUM COUPLED STATES AND SEMI-CLASSICAL CALCULATIONS OF $Q(J)$ ($J = 0, 1, 2$) LINE SHAPE PARAMETERS IN PURE HYDROGEN*
X. BRUET, J. BONAMY, and M.L. DUBERNET-TUCKEY
- O22 – *TEMPERATURE DEPENDENCE OF LINE BROADENING AND LINE SHIFTING IN PURE ROTATIONAL S_0 AND VIBRATIONAL Q BRANCHES OF H_2 IN H_2O*
X. MICHAUT, R. SAINT-LOUP, H. BERGER, J. BONAMY, P. JOUBERT,
D. ROBERT, and J. HUSSONG
- O23 – *WATER VAPOR LINE SHIFTING OF THE $\nu_1 + \nu_2$ END $\nu_2 + \nu_3$ BANDS INDUCED BY O_2 AND Ar PRESSURE*
LAVRENTIEVA N.N., and SOLODOV A.M
- O24 – *BROADENING AND SHIFT BY COLLISIONS WITH ARGON FOR HCO^+ ROTATIONAL LINES*
G. BUFFA, O. TARRINI, G. CAZZOLI, and L. DORE
- O25 – *THE INFRARED SPECTRUM OF CH_3D BETWEEN 900 AND 3200 cm^{-1}*
A. NIKITIN, J.P. CHAMPION, VI.G. TYUTEREV, and L.R. BROWN
- O26 – *ROTATIONAL DEPENDENCE OF GIANT l-DOUBLING IN SYMMETRIC TOP MOLECULES*
MIKHAILOV V.M., and SMIRNOV M.A
- O27 – *ROTATIONAL ANALYSIS OF THE NEAR INFRARED SINGLET-TRIPLET ELECTRONIC SPECTRUM OF OZONE*
A.J. BOUVIER, G. WANNOUS, D. INARD, I. RUSSIER, V. VEYRET, E. BOURSEY, S. CHURASSY, R. BACIS, J. BRION, J. MALICET, and R.H. JUDGE
- O28 – *THE $A^2\Pi - X^2\Sigma^+$ SYSTEM OF THE LaO MOLECULE*
D. CERNY, A.J. BOUVIER, R. BACIS, and A. BERNARD
- O29 – *A DIATOMIC POLAR AND POLARISABLE MOLECULE IN AN ELECTRIC FIELD*
E. BENICHO, A.R.ALLOUCHE, R. ANTOINE, M. AUBERT-FRECON,
M. BOURGOIN, M. BROYER, Ph. DUGOURD, G. HADINGER, and D. RAYANNE
- O30 – *SINGLET STATES OF K_2 CORRELATING WITH THE $K(4s)+K(4p)$ ASYMPTOTE*
I. RUSSIER-ANTOINE, A.J. ROSS, M. AUBERT-FRECON, F. MARTIN,
P. CROZET, S. MAGNIER, H. WANG, and W.C. STWALLEY

- O31 - *HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CHLORYL FLUORIDE, $FCIO_2$*
JEAN-MARIE FLAUD, HOLGER S. P. MÜLLER, and HANS BÜRGER
- O32 - *ABSORPTION AND EMISSION SPECTROSCOPY OF YTTERBIUM IN SOLID ARGON*
IGOR D. REVA, and WERNER E. KLOTZBÜCHER
- O33 - *OBSERVATION OF SEVERAL NEW ELECTRONIC TRANSITIONS OF THE $SiOH$ FREE RADICAL*
MATTHEW S. BEARDAH, and ANDREW M. ELLIS
- O34 - *DEVELOPMENT OF DOUBLE MODULATION SUBMILLIMETER-WAVE SPECTROMETER: DETECTION OF THE LOWEST PURE ROTATIONAL TRANSITION OF CH*
T. AMANO
- O35 - *A FULL DESCRIPTION OF THE POTENTIAL CURVE OF THE $B^1\Pi_u$ STATE OF 7Li_2 , INCLUDING ITS POTENTIAL BARRIER*
N. BOULOUBA, P. CACCIANI, R. VETTER, A. YIANOPOULOU, F. MARTIN, and A. J. ROSS
- O36 - *THE HIGHLY EXCITED VIBRATIONAL DYNAMICS OF HCP , DCP AND $HOCl$*
MARC JOYEUX, DOMINIQUE SUGNY, and REMY JOST
- O37 - *MASS ANALYZED THRESHOLD IONIZATION SPECTROSCOPY OF P -FLUOROANILINE CATION*
WEN-BIH TZENG, and JUNN-LEE LIN
- O38 - *THE MOLECULAR GEOMETRY AND QUADRUPOLE COUPLING CONSTANTS OF $ClPO_2$*
BETHANY BRUPBACHER-GATEHOUSE
- O39 - *THE MICROWAVE SPECTRUM OF 1-CHLORO-2-METHYLPROPENE: METHYL INTERNAL ROTATION AND $^{35,37}Cl$ NUCLEAR QUADRUPOLE COUPLING*
T. BRUHN, and W. STAHL
- O40 - *WAVE PACKET DYNAMICS IN THE GROUND STATES OF DIATOMIC MOLECULES*
NIKOLAI E. KUZ'MENKO, VADIM V. ERYOMIN, and IGOR M. UMAN-SKII

Invited Lectures P, Friday, September 10, 14:00

Chairman : A. TROMBETTI

P1 - *SPECTRA OF VERY WEAKLY BOUND MOLECULAR COMPLEXES*
A.R.W. McKELLAR

P2 - *FREE JET ABSORPTION MILLIMETER WAVE SPECTROSCOPY OF
COMPLEX ROTATIONAL SPECTRA, OF VAN DER WAALS AND OF HY-
DROGEN BONDED ADDUCTS*
W. CAMINATI

Invited Lectures A

Monday, September 6, 9:00

Chairman : M. QUACK

INFRARED CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY

R.J. SAYKALLY, *Department of Chemistry, University of California, Berkeley, CA 94720-1460, USA*

CRLAS has emerged as a powerful and convenient new spectroscopic technique^a capable of measuring weak absorptions (fractional absorption sensitivity ca. 1×10^{-6}) in short times (ca. 10 μ sec). We have recently concentrated on extending this technology into the infrared,^b wherein it has the capability to replace diode, difference frequency, and color center lasers. Recent results for water^c and alcohol clusters^d and plasma generated species will be described.

^aJ.J. Scherer, J.B. Paul, A. O'Keefe, and R.J. Saykally, *Chemical Reviews* 97, 1, 25-51 (1997); J.B. Paul and R.J. Saykally, *Analytical Chemistry* A 69, 287 (1997); R.A. Provencal, J.B. Paul, C.N. Chapo, and R.J. Saykally, *Spectroscopy* 14, 24 (1999).

^bJ.J. Scherer, D. Voelkel, D.J. Rakestraw, J.B. Paul, C.P. Collier, A. O'Keefe, and R.J. Saykally, *Chem. Phys. Lett.* 245, 273-280 (1995).

^cJ.B. Paul, R.A. Provencal, and R.J. Saykally, *J. Phys. Chem. A* 102, 3279 (1998); J.B. Paul, R.A. Provencal, C. Chapo, A. Pettersson, and R.J. Saykally, *J. Chem. Phys.* 109, 10201 (1998); J.B. Paul, R.A. Provencal, C. Chapo, K. Roth, R. Casaes, and R.J. Saykally, *J. Phys. Chem. A* 103, 2972 (1999); C.J. Chapo, J.B. Paul, R.A. Provencal, K. Roth, and R.J. Saykally, *J. Am. Chem. Soc.* 120, 12956-12957 (1998).

^dR.A. Provencal, J.B. Paul, K. Roth, C. Chapo, R.N. Casaes, R.J. Saykally, G.S. Tschumper, and H.F. Schaefer, III, *J. Chem. Phys.* 110, 4258 (1999).

NEW DEVELOPMENTS OF INTRACAVITY ABSORPTION
SPECTROSCOPY:
APPLICATION TO THE CH ACETYLENIC OVERTONE
TRANSITIONS OF PROPYNE

A. CAMPARGUE, *Laboratoire de Spectrométrie Physique (CNRS UMR 5588), Université J. Fourier de Grenoble, B.P. 87, 38402 Saint Martin d'Hères Cedex, France, Alain.Campargue@ujf-grenoble.fr*

Intracavity Laser Absorption Spectroscopy (ICLAS) has a 30 year history and has experienced a slower development than the younger and more popular Cavity Ring Down Spectroscopy (CRDS) technique (see ^a for a recent review). Compared to other high sensitivity laser absorption techniques ICLAS has, however, an unique feature, highly valuable for studies over a large spectral regions: the spectral multiplex advantage resulting in an increase in data acquisition speed. Recent developments achieved, in particular by A. Kachanov *et al.*, include the detection of the ICLAS spectrum by a Fourier Transform Spectrometer ^b and the development of a new ICLAS spectrometer based on a multiple quantum well structure in a VECSEL configuration ^c.

The second part of the talk will be devoted to the high resolution absorption spectroscopy of the $\nu_1 = 2-6$ acetylenic overtone bands of propyne^d ($\text{CH}_3\text{-C}\equiv\text{C-H}$) which were recorded by using Fourier Transform Spectroscopy ($\nu_1 = 2$), various Intracavity Laser Absorption Spectrometers ($\nu_1 = 3, 4$ and 6) and Cavity Ring Down Spectroscopy (CRDS) ($\nu_1 = 5$). The $5\nu_1$ band shows an unresolved rotational envelope while the $2\nu_1$, $3\nu_1$ and $6\nu_1$ bands exhibit a well-resolved and mostly unperturbed J -rotational structure, whose analysis is reported. In the region of 12700 cm^{-1} , an anharmonic interaction is confirmed between $4\nu_1$ and $3\nu_1 + \nu_3 + \nu_5$. The band at higher wavenumber in this dyad exhibits a partly resolved K -structure. The mixing coefficient of the two interacting states is determined consistently using different procedures. The $1/35$ anharmonic resonance, observed in the $4\nu_1$ manifold, induces weaker intensity borrowing from the $2\nu_1$ and $3\nu_1$ levels to the $\nu_1 + \nu_3 + \nu_5$ and $2\nu_1 + \nu_3 + \nu_5$ level respectively which have been predicted and identified. Several hot bands around the $2\nu_1$, $3\nu_1$ and $3\nu_1 + \nu_3 + \nu_5$ bands arising from the $\nu_9 = 1$ and $\nu_{10} = 1$ and 2 bending levels are identified and rotationally analysed,

^aM. Herman, J. LiÈvin, J. Vander Auwera and A. Campargue, *Adv. Chem. Phys.* Vol.108 (1999) pages 1-431

^bJ. Cheng, H. Lin, S. He, Q. Zhu and A. Kachanov submitted to *Chem. Phys. Lett.*

^cA. Garnache, A.A. Kachanov, F. Stoeckel and R. Planel. *Optics Letters* 000 (1999) 000

^dA. Campargue, L. Biennier, A. Garnache, A. Kachanov D. Romanini and M. Herman submitted to *J. Chem. Phys.*

also leading to determine $x_{1,9}$, $x_{1,10}$ and $x_{3,10}$. The J -clumps of the P and R branches in the $6\nu_1$ band at 18499 cm^{-1} show a Lorentzian homogeneous profile mostly J -independent with an average FWHM of 0.17 cm^{-1} , arising from the intramolecular vibrational energy redistribution towards the bath of vibrational states. A detailed comparative examination of the fine structure in all investigated overtone bands and the similar behaviour of the cold and hot bands arising from $\nu_{10}=1$ definitively suggests that a highly specific low order anharmonic coupling, dominates the hierarchy of interaction mechanisms connecting the $n\nu_1$ levels to the background states.

Poster Session B
Monday, September 6, 11:00

CW-DIODE-LASER CAVITY-RING-DOWN SPECTROSCOPY OF NITROUS OXIDE AND METHANE IN PULSED SUPERSONIC SLIT JETS

MICHAEL HIPPLER, MARTIN QUACK, *Laboratorium für
Physikalische Chemie, ETH Zürich (Zentrum), CH-8092 Zürich, Switzerland*

We have recently reported a fairly simple approach to CW-cavity-ring-down (CW-CRD) rovibrational spectroscopy of polyatomic molecules employing a high-resolution near-infrared diode laser ^a. Such studies are of interest for the analysis of the rovibrational quantum dynamics of polyatomic molecules and clusters ^b. While such an application for a Fermi resonance analysis of the vibrational overtone spectrum of chloroform was indeed possible with CW-CRD spectra of room temperature samples, the full potential of the method at high resolution (1 MHz effective instrumental function) becomes available only in measurements in supersonic jets ^c. We report the first experimental set-up combining CW-CRD with a pulsed slit nozzle expansion and demonstrate this new technique with rovibrational overtone spectra of nitrous oxide and methane in a supersonic jet.

We show the outstanding possibilities of the technique also for other polyatomic molecules as well as for the analysis of complex high overtone bands in the examples mentioned.

^aY. He, M. Hippler and M. Quack, *Chem. Phys. Lett.* 289 (1998) 527-534.

^bM. Quack, chapter 27 in "Femtosecond Chemistry", J. Manz, L. Woeste, eds., Verlag Chemie, Weinheim (1995), p. 781-818.

^cM. Hippler and M. Quack, in preparation.

CAVITY RING-DOWN SPECTROSCOPY WITH MID-INFRARED CW LASERS FOR ATMOSPHERIC TRACE GAS DETECTION

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für Angewandte Physik, Universität Bonn, D-53115 Bonn, Germany*

Cavity ring-down spectroscopy (CRDS) is one of the most sensitive methods to obtain absorption spectra of diluted gas samples. Although CRDS is widely employed for high-sensitivity spectroscopy from the ultraviolet to the near-infrared, this technique has found less applications in the mid-infrared, mainly due to the lack of high-reflectivity mirrors and due to poor photodetector performance.

In this work we investigate the performance of a mid-infrared CRDS setup for atmospheric trace gas detection. An external high-finesse cavity is excited on a single fundamental mode with a tunable cw laser. After excitation, the laser power is turned off for a short time and the subsequent decay of the radiation stored in the cavity is observed and analyzed. This cw approach has several advantages compared with the conventional pulsed CRDS scheme. First, the spectral resolution achieved is much higher. Moreover, a large fraction of the laser light is transmitted through the absorption cell to the photodetector, whereas with pulsed CRDS most of the incident laser light is wasted by reflection at the input mirror. This enables the utilization of low-power mid-infrared laser sources ($P < 100 \mu\text{W}$).

Our experiments have been carried out with a CO overtone sideband laser in the wavelength region around $3 \mu\text{m}$. The ring-down mirrors used have a reflectivity of $R = 99.98\%$ which results in an effective absorption pathlength of about 5 km. The minimum detectable absorption coefficient we achieved is in the order of $10^{-8}/\text{cm}$ with a typical averaging time of 2 s. We applied our setup for the detection of trace amounts of various hydrocarbons, e. g., methane, ethane, in atmospheric air at the ppb level. The experimental approach and results are reported.

This work is supported by the German Federal Foundation for Environmental Research (Deutsche Bundestiftung Umwelt).

Reference:

M. Mürtz, B. Frech, and W. Urban, *Appl. Phys. B* 68, 243 (1999).

**JET-DISCHARGE CAVITY RINGDOWN SPECTROSCOPY OF
IONIZED POLYCYCLIC AROMATIC HYDROCARBONS:
PROGRESS IN TESTING THE PAH HYPOTHESIS FOR THE
DIFFUSE INTERSTELLAR BAND PROBLEM**

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Space Science Division, MS 245-6, Moffett Field, CA 94035-1000, USA*

Naphthalene cations ($C_{10}H_8^+$) were produced in a slit jet coupled with an electronic discharge, and cavity ring down was used to obtain its absorption spectrum in the region 645–680 nm. Two of the strongest $C_{10}H_8^+$ bands previously characterized by matrix isolation spectroscopy (MIS) were found, both with a fractional blue shift of about 0.5%. To our knowledge, this is the first gas-phase electronic absorption spectrum of an ionized polycyclic aromatic hydrocarbon (PAH). This work opens the way for a direct comparison of laboratory PAH spectra with the diffuse interstellar bands (DIBs), whose origin still constitute an open problem in astrophysics.

HIGH RESOLUTION PHOTOACOUSTIC AND FTIR OVERTONE SPECTRA OF DIACETYLENE

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University of Helsinki, Finland;* WOLFGANG JERZEMBECK and
HANS BÜRGER, *Anorganische Chemie, FB 9,
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We have recorded high resolution vibration-rotation spectra of diacetylene (HCCCCH) in the 6000 cm^{-1} to 14500 cm^{-1} wavenumber region. The photoacoustic measurements have been carried out with a titanium:sapphire ring laser (Coherent 899-21) spectrometer at a Doppler-limited resolution of about 0.02 cm^{-1} . The FTIR measurements have been performed with a Bruker IFS 120 HR at a resolution of about 0.01 cm^{-1} . A multipass cell with an optical pathlength up to 20 meters has been used in the FTIR studies. The overtone spectrum of diacetylene shows rich fine structure due to hot bands and rovibrational resonances. Due to these resonances and due to the small rotational constant, the photoacoustic spectrum of diacetylene becomes rotationally unanalysable at the third overtone C-H stretching region.

**SPECTROSCOPIC INVESTIGATION OF
VIBRATION-ROTATION BANDS IN ACETALDEHYDE:
FOCUS ON $n\nu_3$ ($n=1-5$) ALDEHYDE CH STRETCH BANDS^a**

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Lasers, Atomes et Molécules, UMR CNRS, Centres d'Etudes et de
Recherches Lasers et Applications, Université des Sciences et Technologies de
Lille, F-59655 Villeneuve d'Ascq Cédex, France; and I. KLEINER,
*Laboratoire de Photophysique Moléculaire, Bât 213, Université Paris Sud,
F-91405 Orsay Cédex, France**

We describe experiments on acetaldehyde ($^{12}\text{CH}_3$ $^{12}\text{CH}^{16}\text{O}$) resulting in new or improved spectroscopic data on the $n\nu_3$ ($n=1-5$) aldehyde CH stretching vibrational bands. The $n=1$ component is rotationally resolved using room temperature and supersonic jet Fourier transform spectroscopy, and vibration-rotation assignments are reported. The next two components ($n=2,3$) are recorded at room temperature using Fourier transform spectroscopy and the K -structure is resolved and assigned. The last two series of bands ($n=4,5$) are observed but not resolved, using laser optoacoustic spectroscopy. Effective vibrational constants ($\omega_3^{\text{eff}} = 2938.53 \text{ cm}^{-1}$, $x_{33}^{\text{eff}} = 55.75 \text{ cm}^{-1}$) are obtained. Information is also provided on additional bands in the spectrum from 1300 to 14000 cm^{-1} , involving, in particular, the assignment of the K -structure in ν_{11} and $2\nu_1$, from the jet cooled and the room temperature Fourier transform spectral data, respectively.

^aWe dedicate this work to the memory of Ikhlef Hadj Bachir

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FAST PHASE-SELECTIVE DETECTION OF TRANSIENT SPECIES WITH STEP-SCAN FOURIER TRANSFORM SPECTROSCOPY

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Selective detection techniques in FTS have already been demonstrated with step-scan interferometers^a and have produced original results with rapid-scan interferometers^b. Recently high resolution double-modulation FT emission spectra of molecular ions, created in a glow discharge, with velocity modulation^c as a source modulation have been reported^d.

The recording of a high resolution step-scan Fourier interferogram lasts often several hours. This is therefore prohibitive in the preparation phase of an experiment, when searching for the appropriate source conditions to produce transient species. Since high maximum path-difference is usually needed to provide the phase-modulated information (the phase-modulated lineshift is generally of the order of 10^{-3} cm^{-1} around 2500 cm^{-1} , corresponding to $\Delta=250 \text{ cm}$), it seems impossible to optimize the production of the species of interest with FTS.

We report a new approach, based on the double-modulation FTS technique, to obtain in a few minutes, the selective and nonselective spectra of the source under test. It consists of recording only an identical small portion at high path difference of both interferograms. The Fourier transform of this limited part of the interferograms is practiced with no care of the phase. The spectral resolution, of the order of 0.1 cm^{-1} , corresponds to a virtual maximum path difference equal to the path-difference excursion actually explored, and the spectral range can extend over several thousands of cm^{-1} , as it is usual with FTS. Comparison of the selective and nonselective spectra provides an unambiguous recognition of the nature of the species present in the plasma. As a demonstration, spectra of the $\Delta v = 1$ sequence vibration-rotation bands

^aG. Guelachvili, *Journal of the Optical Society of America B* **3**, 1718-1721, 1986.

N. Picqué, G. Guelachvili, *Applied Optics* **38**, 1224-1230, 1999, and references therein.

^bX. Hong, and T.A. Miller, *Chemical Physics* **228**, 131-144, 1998, and references therein.

^cC.S. Gudeman, M.H. Begeman, J.Pfaff, and R.J. Saykally, *Physical Review Letters* **50**, 727-731, 1983.

^dNathalie Picqué, Guy Guelachvili, *Vibrational Spectroscopy* **19**, 295-299, 1999.

of velocity-modulated ArH^+ in the 2500 cm^{-1} region are presented. First attempts to observe ionic species in C, N, H containing electrical discharges are also reported.

DOPPLER-SHIFT MEASUREMENTS AND INVESTIGATION OF THE STATE-TO-STATE DEPENDENCE OF THE ArH^+ ION AVERAGE MOBILITY IN A Ar/He PLASMA

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Results aiming at characterizing the transport properties and the abundance of ions in plasmas are reported. As an illustration, the quantum dependence of the average mobility of ArH^+ in an Ar/He mixture in an inhomogeneous electric field has been investigated^a: no vibrational nor rotational energy dependence of the ArH^+ ion average mobility in an inhomogeneous electric field is observed, within an experimental uncertainty of 5 %. It is obtained from Doppler-shifts measured in emission spectra of the $\Delta v=1$ sequence vibration-rotation bands of ArH^+ around 2500 cm^{-1} , thanks to Multi-Modulation Fourier Transform Spectroscopy^b, with velocity modulation^c as a selective modulation. The results are compared to those extracted from line positions measurements in successive FT spectra with opposite dc discharge polarities, in order to validate the new method. This first demonstration extends to wide-band spectroscopy the measurements pioneered by Haese, Pan, and Oka^d with diode-lasers, in similar source conditions.

^aN. Picqué, Wide-band spectroscopic investigation of the state-to-state dependence of ArH^+ ion average mobility in a Ar/He plasma, *Chemical Physics Letters*, 1999 (submitted).

^bN. Picqué, G. Guelachvili, High resolution multi-modulation Fourier transform spectroscopy, *Applied Optics* **38**, 1224-1230, 1999.

^cC.S. Gudeman, M.H. Begeman, J.Pfaff, and R.J. Saykally, Velocity modulated infrared laser spectroscopy of molecular ions: the ν_1 band of HCO^+ , *Physical Review Letters* **50**, 727-731, 1983.

^dN.N. Haese, F-S. Pan, and T. Oka, Doppler shift and ion mobility measurements of ArH^+ in a He dc glow discharge by infrared laser spectroscopy, *Physical Review Letters* **50**, 1575-1578, 1983.

ROVIBRATIONAL ANALYSIS OF THE ν_6 BANDS OF FOUR ISOTOPOMERS OF FCIO_3

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High resolution (ca. $5 \times 10^{-3} \text{ cm}^{-1}$) infrared spectra of monoisotopic samples of $\text{F}^{35}\text{Cl}^{16}\text{O}_3$, $\text{F}^{37}\text{Cl}^{16}\text{O}_3$, $\text{F}^{35}\text{Cl}^{18}\text{O}_3$, and $\text{F}^{37}\text{Cl}^{18}\text{O}_3$, have been recorded in the region of the ν_6 fundamental band. This band is centered at 405.6055, 405.5097, 390.5406, and 390.4984 cm^{-1} respectively. About 1000 non zero-weighted transitions were fitted for each isotopomer with an isolated band model, obtaining a s.d. on the residuals close to the experimental precision.

Three different reductions ^{a,b} of the Hamiltonian have been tested and found almost equally good, although FCIO_3 is a nearly-spherical top molecule. Each include the $l(2,2)$ interaction and either a $d_t \Delta K = \pm 3$ interaction term (reduction Q), or an $\epsilon_t \Delta K = \pm 3$ interaction term (reduction QD), or a $l(2,-1)$ interaction (reduction D). Good agreement between the theoretical predictions for these reductions and the experimental data is observed.

^aJ.K.G. Watson, C. Gerke, H. Harder, and K. Sarka, *J. Mol. Spectrosc.*, **187**, 131-141(1998)

^bH.Harder *J. Mol. Spectrosc.*, **194**,145(1999)

THE $\nu_6=2$ STATES OF FCIO_3

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In a previous study, we have analysed the ν_6 fundamental band of the 4 isotomers of FCIO_3 , with three different reduced hamiltonians. A recent theoretical work ^a on the $\nu_t=2$ states of C_{3v} molecules prompted us to study the $\nu_6=2$ states of FCIO_3 . We had to study IR spectra (resolution ca. $5 \times 10^{-3} \text{ cm}^{-1}$) in two different regions. In the $2\nu_6$ overtone region ($750\text{-}805 \text{ cm}^{-1}$), the parallel component $2\nu_6^0$ is relatively easy to assign up to $J=85$ and $K=60$ but the perpendicular component $2\nu_6^{\mp 2}$ cannot be observed at all. In the ν_6 region, one can find several $^R R$ and $^P P$ series of the hot band $2\nu_6^{\pm 2} - \nu_6^{\pm 1}$ although they are often blended.

The model adopted to fit the data takes into account a $l(2,2)$ interaction, two $\Delta K = \pm 3$ interactions with parameters ϵ_t and d_t but ϵ_t was kept fixed to the ground state value. It uses also a $l(2,-1)$ interaction, with a parameter q_{12} mostly defined by the local perturbation found between the sublevels ($K=9, l=0$) and ($K=8, l=2$).

At present, all data can be fitted with a s.d. of residuals of ca. $0.3 \times 10^{-3} \text{ cm}^{-1}$ for the two isotomers $\text{F}^{35}\text{Cl}^{18}\text{O}_3$ and $\text{F}^{37}\text{Cl}^{18}\text{O}_3$. We hope to be able to report also some results concerning the isotomers with ^{16}O .

^aK. Sarka and H. Harder, *J. Mol. Spectrosc.*, in press

**SUB-DOPPLER POLARIZATION SPECTROSCOPY OF THE
 $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ SYSTEM FOR Cs_2 WITH A TITANIUM
SAPPHIRE LASER**

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Sub-Doppler spectrum of the $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ system for Cs_2 was observed by the polarization spectroscopic method with a titanium sapphire laser in the region from 12 800 to 13 200 cm^{-1} . Cesium vapor was produced by heating in a stainless steel heat pipe cell. The cell of 1 m length was heated at 670 K with argon buffer gas. In order to avoid stacking Cs atoms at the windows, water tanks were set at both ends of the cell. The effective absorption length was 40 cm. The residual transmission of the probe beam was estimated to be as small as 10^{-6} of the input probe beam intensity. The spectral line width was 140 MHz in the HWHM. The *P*-, *R*- and *Q*-branch lines were observed because of the high resolving power and of the selection of polarized conditions. In our previous report only *Q*-branch lines were assigned by the Doppler limited absorption spectroscopy, since the spectral lines are very dense in this region^a.

The vibrational bands $v' = (0 - 12) \leftarrow v'' = (0 - 8)$ were measured and 8,300 lines could be assigned. The sixteen Dunham coefficients of *B* state were determined by the least-squares fitting procedure with the aid of the *X* state Dunham coefficients reported by Weickenmeier *et al.*^b The standard deviation was 0.0016 cm^{-1} . The rotational levels of spectral lines were up to $J = 250$. The details of the results will be presented.

^aT. Yukiya, M. Satoh, N. Nishimiya and M. Suzuki *53rd. International Symposium on Molecular Spectroscopy*, pp.265 June 1998.

^bW. Weickenmeier, U. Diemer, M. Wahl, M. Raab, W. Demtröder and W. Müller *J. Chem. Phys.* **82**(12), pp.5354 June 1985.

**HIGH - RESOLUTION LASER SPECTROSCOPY OF THE
 $A^3\Pi_1 \leftarrow X^1\Sigma^+$ SYSTEM OF IBr WITH A
 TITANIUM:SAPPHIRE RING LASER**

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The vib-rotational absorption spectrum of the $A^3\Pi_1 \leftarrow X^1\Sigma^+$ system in $I^{79/81}\text{Br}$ was observed in the 11200 to 13300 cm^{-1} region using a Ti:sapphire ring laser.

The P , Q and R -branch lines of $J=10$ to 100 belonging to the $v' \leftarrow v'' = (3 \sim 20) \leftarrow (1 \sim 6)$ progressions were assigned. The hyperfine splittings caused by the nuclear spin coupling effects were resolved in the P and R branches, while no splittings occurred in the Q -branch lines. Using a formula based on a first order perturbation theory where the eQq'_1 and eQq'_2 of I atom were taken into consideration, the unperturbed line positions were determined for the higher rotational transitions of $J = 10$.

The line frequencies in the far infrared region reported by J. M Campbell and P. F. Bernath^a were combined with the X state combination differences calculated from the unperturbed line positions, and the Dunham coefficients of $Y''_{1,0}$, $Y''_{2,0}$ and $Y''_{3,0}$ were determined using a least squares fitting procedure. The rotational parameters were constrained to those reported by R. E. Willis, Jr. and W. W. Clark, III^b in this fitting.

Using the vibrational constants thus obtained and the rotational parameters by ref^b, the Dunham coefficients of the A state were then calculated. The standard deviations and those errors rather increased and the calculated line positions deviated from the observed ones, when the lines related to the lower vibrational states of $v' = 6$ were combined for the least squares analysis.

Although D. R. T. Appadoo et. al.^c have determined the higher order terms Y_{l0} ($l = 0 \sim 10$) and Y_{l1} ($l=0 \sim 7$), we used the spectroscopic constants of T'_v , $B'_{ve/ff}$, D'_v and H'_v to describe the vib-rotational levels from $v' = 3$ to 20 for the A state. The details of the analysis will be presented.

^aJ. M Campbell and P. F. Bernath *J. Mol. Spectrosc.* **158**, 339-346 (1993).

^bR. E. Willis, Jr. and W. W. Clark, III *J. Chem. Phys.* **72**(9), 4946-4950(1980).

^cD. R. T. Appadoo, P. F. Bernath and R. J. Le Roy *Can. J. Phys.* **72**, 1265-1272 (1994).

DIODE-LASER MEASUREMENTS OF N₂-BROADENING COEFFICIENTS IN THE ν_7 BAND OF C₂H₄

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In this work, we have measured the N₂-broadening coefficients of 35 lines in the ν_7 band of C₂H₄, using a tunable diode-laser spectrometer. Most of these lines were sufficiently isolated to be individually fitted by Voigt and Rautian lineshape models from which their collisional widths have been derived. However, for some lines where the overlapping with neighboring lines could not be disregarded, we used a fit of superposed Voigt or Rautian profiles by neglecting the collisional interference between the lines.

A calculation of the broadening coefficients has been performed on the basis of the semiclassical model developed in Ref. ^a by assuming that C₂H₄ may be approximated to a prolate symmetric top molecule. The quantum number J'' and dependencies of the broadening coefficients obtained experimentally are finally compared with theoretical predictions.

^aJ.P. Bouanich, G. Blanquet, and J. Walrand, *J. Mol. Spectrosc.* 161, 416-426 (1993).

HIGH RESOLUTION SPECTRA OF CARBON DISULFIDE $^{12}\text{C}^{32}\text{S}_2$ IN THE REGION OF $2\ \mu\text{m}$

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The aim of the present work is a reinvestigation, with high resolution Fourier transform spectrometer, of the spectral region between 5100 and 5600 cm^{-1} . The higher resolution provided by this spectrometer yields a great improvement in the analysis of the $10^0_3 - 00^0_0$ band. We also observed new transitions: the hot bands associated $11^1_3 - 01^1_0$, $20^0_3 - 10^0_0$, the isotopic band $10^0_3 - 00^0_0$ of $^{12}\text{C}^{32}\text{S}^{34}\text{S}$. Due to the very good S/N ratio of the spectrometer, the very weak transition $02^0_3 - 00^0_0$ has been observed. Moreover a very small perturbation has been detected in the $\nu_1 + \nu_3$ band around $J = 80$ and has been attributed to a resonance between the 10^0_3 and 18^0_1 levels.

In order to record these weak bands, we have been forced to use relatively high gas pressure approximately 40 mbar in the absorption cell. For such a pressure, the effective resolution is no more given by the Doppler width because the collisional broadening is increased. A preliminary study has been realized to determine the broadening coefficient for self-broadening of CS_2 . These measurements have been made for two lines of the $\nu_3 - \nu_1$ band with a tunable diode laser (TDL). The determined self-broadening coefficient γ_0 is of the order of $0.120\ \text{cm}^{-1} \cdot \text{atm}^{-1}$.

THE GROUND STATE ROTATIONAL SPECTRA OF H_2^{13}CO AND $\text{H}_2\text{C}^{18}\text{O}$

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H_2CO is a molecule highly abundant in interstellar space. Besides the main isotopomer, the HD, D_2 , ^{13}C , and ^{18}O isotopomers have been detected. Although formaldehyde is one of the most studied molecules by means of rotational spectroscopy, we found that the published parameters are not accurate enough for a reliable prediction of the millimeter wave spectrum. This prompted us to remeasure the rotational spectrum of H_2CO ,^a HDCO, and D_2CO ^b from the microwave to the far infrared region (2.5 THz). As a continuation of this project, we have started to remeasure the rotational spectra of H_2^{13}CO and, in Cologne only, of $\text{H}_2\text{C}^{18}\text{O}$. At present, we have used only samples in natural isotopic composition. It is intended to use a sample highly enriched in ^{13}C .

In Kiel, waveguide microwave Fourier transform spectrometers are used to cover the regions 18–26 and later 1–4 and 8–18 GHz. The Cologne Terahertz Spectrometer was used to cover the region of 530–840 GHz; higher frequency measurements are intended. The stronger, well isolated lines are accurate to 10–20 kHz. In Lille, measurements have begun to cover the 1–2.5 THz region. The accuracy of the measurements is better than 300 kHz when the laser is stabilized. The number of assigned transitions was greatly increased. Accurate molecular parameters will be reported, and the convergence of the Hamiltonian (in *A*- and *S*-reductions) will be discussed briefly.

^aR. Bocquet, J. Demaison, L. Poteau, M. Liedtke, S. P. Belov, K. M. T. Yamada, G. Winnewisser, C. Gerke, J. Gripp, and Th. Köhler, *J. Mol. Spectrosc.* **177** (1996) 154.

^bR. Bocquet, J. Demaison, J. Cosleou, A. Friedrich, L. Margules, S. Macholl, H. Mäder, M. M. Beaky, and G. Winnewisser, *J. Mol. Spectrosc.* **195** (1999) 345.

THE $\nu_3 = 1$ STATE OF HSiF_3 AND DSiF_3 STUDIED BY HIGH
RESOLUTION INFRARED AND MILLIMETERWAVE
SPECTROSCOPY

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High resolution FTIR spectra ($\sigma = 2.4 \times 10^{-3} \text{ cm}^{-1}$) of HSiF_3 and DSiF_3 in the region of the parallel-type ν_3 band, $\nu_0 = 424.07 \text{ cm}^{-1}$ and 420.93 cm^{-1} , respectively, have been recorded and analyzed. Owing to the smallness of $\alpha^B - \alpha^C$, ca. $-1.4 \times 10^{-5} \text{ cm}^{-1}$, $^Q P$ and $^Q R$ clusters are too narrow for low J values to be resolved into their K components but exhibit resolved K structure for $J > \approx 20$ in the P and $J'' > \approx 30$ in the R branches. This K -structure is however due to effects of D_{JK} and hence extends into opposite directions in the $^Q P$ and $^Q R$ clusters, respectively. While the structure of the hot bands $\nu_3 + \nu_6 - \nu_6$ grossly resembles that of ν_3 , the hot bands $2\nu_3 - \nu_3$ look different because of a strong anharmonic perturbation of $2\nu_3$ by ν_2 . The pure rotational spectrum has been measured from 148 GHz to 473 GHz with a spectrometer using backward-wave oscillators as sources and a He-cooled InSb bolometer as detector.

The IR-transitions with J''_{max} and $K_{max} = 75$ and 57, respectively, and millimeterwave transitions with $10 \leq J \leq 31$ (HSiF_3) and $10 \leq J \leq 33$ (DSiF_3) were fitted together, with appropriate weighting, and parameters up to sextic centrifugal distortion terms of the unperturbed $\nu_3 = 1$ states have been determined.

**ROVIBRATIONAL SPECTROSCOPY
OF THE $\nu_5=1$ LEVEL OF $^{28}\text{SiDF}_3$**

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The ν_5 fundamental band of trifluorosilane-*d* (SiDF_3) at 627 cm^{-1} was studied for the first time by high resolution FTIR spectroscopy at a resolution of $2.4 \times 10^{-3}\text{ cm}^{-1}$. The analysis was performed simultaneously with available microwave and newly measured submillimeter wave data in the approximation of an isolated degenerate fundamental level of a C_{3v} symmetric top molecule leading to a standard deviation of $0.22 \times 10^{-3}\text{ cm}^{-1}$ for the reproduction of the infrared wavenumbers, 36 kHz for the microwave and 198 kHz for the submillimeter wave frequencies, respectively. The relations between the two reductions (Q and D) of the effective Hamiltonian applied in the analysis are discussed.

ROTATIONAL ANALYSIS OF THE ν_2 BAND OF DIAZIRINE-d₂ FROM HIGH RESOLUTION FTIR SPECTRA

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The high resolution FTIR spectrum of deuterated diazirine, D₂CN₂, has been recorded at Doppler limited resolution ($\approx 0.005 \text{ cm}^{-1}$) in the region of the ν_2 fundamental (1610 cm^{-1}).

This molecule, an asymmetric top rotor with $\kappa = -0.6274$, belongs to the C_{2v} point group. The ν_2 vibrational mode, of symmetry species A₁, which can be approximately described as N=N stretch, gives rise to an a-type rotational band envelope. The corresponding band of the parent species is strongly perturbed by a Fermi resonance with the $2\nu_7$ overtone. This perturbation is removed in the present isotopomer due to the lowering of the ν_7 fundamental; nevertheless other perturbative effects had to be taken into account during the assignment of the rovibrational transitions. In particular, the band investigated has been found affected by c-type Coriolis resonance with the nearby state $\nu_5 + \nu_9$ of symmetry species B₁ centered at 1601 cm^{-1} .

More than 500 transitions have been assigned with $J \leq 40$ and $K_a \leq 8$. Excited state constants up to quartic terms have been obtained for the ν_2 fundamental band using Watson's A-reduction Hamiltonian in the I' representation including the Coriolis coupling matrix elements. The simultaneous analysis allowed us to determine also the band origin and the rotational constants of the perturber $\nu_5 + \nu_9$ together with the coupling constant ξ_{259}^c .

Details of the interpretation and results obtained from the analysis will be presented.

**FTIR SPECTROSCOPY OF BrCN ISOTOPOMERS IN THE
REGION OF THE $2\nu_3$ BAND: AN IMPROVED EVALUATION
OF THE ANHARMONIC FORCE FIELD
OF CYANOGEN BROMIDE**

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The $2\nu_3$ overtone band of six different isotopomers of cyanogen bromide has been recorded in the range from 4200 to 4400 cm^{-1} using a FTIR spectrometer with an effective resolution of 0.02 cm^{-1} . The following band origins and upper state rotational parameters were obtained:

	ν_0 (cm^{-1})	B (MHz)	D (kHz)
$^{79}\text{Br}^{12}\text{C}^{14}\text{N}$	4371.15692(26)	4079.3789(93)	0.8829(18)
$^{81}\text{Br}^{12}\text{C}^{14}\text{N}$	4371.09158(25)	4056.1001(93)	0.8510(19)
$^{79}\text{Br}^{13}\text{C}^{14}\text{N}$	4271.03900(25)	4035.0180(66)	0.8617(10)
$^{81}\text{Br}^{13}\text{C}^{14}\text{N}$	4270.97473(27)	4011.4864(74)	0.8487(12)
$^{79}\text{Br}^{12}\text{C}^{15}\text{N}$	4314.14732(21)	3905.2261(69)	0.7923(12)
$^{81}\text{Br}^{12}\text{C}^{15}\text{N}$	4314.07505(23)	3882.3788(73)	0.7797(12)

The newly determined band origins have been used, together with previous data, to calculate the quartic force field of cyanogen bromide. The usual second-order perturbation theory has been used to relate the spectroscopic observations to the potential constants, but a variational approach was used to treat the Fermi resonance between the $v_1, v_2^{|l|}, v_3$ and $v_1 - 1, v_2 + 2^{|l|}, v_3$ states. A total number of 12 potential constants were fitted to a set of 78 experimental data, including vibrational energy levels, vibration-rotation α constants, quartic centrifugal distortion constants and q l -doubling constants. The high-order vibrational dependence of the off-diagonal Fermi resonance matrix elements was taken into account in a parametric form. *Ab initio* computed force constants were used to constrain the potential terms which are not directly determinable from the experimental data.

EXTREMELY HIGH ROTATIONAL EXCITATION OF CO IN A DISCHARGE THROUGH COLD CO

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Infrared emission from ^{12}CO and ^{13}CO , excited in the cathode region of a discharge tube immersed in liquid nitrogen, was recorded by Fourier-transform spectrometry at a resolution of 0.005 cm^{-1} . The $\Delta v = 1$ sequence bands recorded from 2500 to 1800 cm^{-1} , indicate the existence of three different rotational populations : i) molecules in the zero-ground level with $T_{rot} \approx 100\text{ K}$ (responsible of reabsorption of part of the 1-0 emission band) ; ii) molecules with $T_{rot} \approx 275\text{ K}$ (maximum intensity for $J'_{max} \approx 6$ in each band, $T_{vib} \approx 3000\text{ K}$ for $v' = 2-4$, $T_{vib} \approx 8600\text{ K}$ for $v' = 5-13$) ; iii) molecules with v' limited to 6, R-rotational lines observed for J' between 60 and 120 ($J'_{max} \approx 90$), non-boltzmanian population distribution. The full-width at half-maximum (FWHM) of all the observed lines is less than 0.0070 cm^{-1} corresponding to a Doppler width of 0.005 cm^{-1} (translational temperature about 270 K). Such high-J levels of the CO molecule had never been observed in the laboratory. In the absorption spectrum of the Sun photosphere, the same lines present FWHM values 6 to 10 times larger ^a. The best available Dunham coefficients ^b are checked to reproduce the high-J lines wavenumbers to at least 0.001 cm^{-1} . Dissociative recombination of the dimer cation $(\text{CO})_2^+$, which is likely to be formed in our experimental conditions, is discussed as a possible mechanism to produce CO fragments with very high rotational excitation, while keeping vibrational excitation limited to $v' = 6$.

^aR. Farrenq, G. Guelachvili, A.J. Sauval, N. Grevesse and C.B. Farmer, *J. Mol. Spectrosc.* **149**, 375-390 (1991)

^bT. George, W. Urban and A. Le Floch, *J. Mol. Spectrosc.*, **165**, 500-505 (1994) ; R. Farrenq, private communication, Orsay, France (1999).

**A PRELIMINARY STUDY IN CH₃SiD₃ OF THE HOT BAND
($v_{12} = 1, v_6 = 1$) \leftarrow ($v_{12} = 0, v_6 = 1$)**

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The hot band ($v_{12} = 1, v_6 = 1$) \leftarrow ($v_{12} = 0, v_6 = 1$) in CH₃SiD₃ has been recorded with Fourier transform spectroscopy to investigate torsional dependency of the molecular parameters in an excited vibrational state. Here, v_{12} and v_6 , respectively, are the principal quantum numbers for the lowest lying degenerate normal vibration and the large amplitude vibration. The measurement was carried out in a room temperature with instrumental resolution of 0.00125 cm^{-1} . More than 1000 lines with $K\Delta K_{\text{max}} = \pm 12$ and $J_{\text{max}} = 40$ were identified and added to the data set that consists of the previous measurements of the fundamental band ($v_{12} = 1, v_6 = 0$) \leftarrow ($v_{12} = 0, v_6 = 0$), torsional bands ($v_6 = 2 \leftarrow 0$), ($v_6 = 3 \leftarrow 1$), and the millimeter-wave measurements in the ($v_6 = 0, 1, 2, 3$) and ($v_{12} = 1$) states. In this work, we report the assignment of the transitions and a preliminary analysis of the hot band.

MEASUREMENTS OF ROTATIONAL TRANSITIONS OF RARE CO ISOTOPOMERS

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High resolution measurements of the $J=2\leftarrow 1$ to $J=6\leftarrow 5$ rotational transition (220-661 GHz) of the carbon monoxide (CO) isotopomers $^{12}\text{C}^{18}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{13}\text{C}^{18}\text{O}$ were performed using phase stabilized backward wave oscillators (BWOs). For the two ^{13}CO isotopomers, the hyperfine splitting due to the carbon nuclear spin-rotation (NSR) interaction could be resolved for the first time leading to the determination of the NSR interaction constant C_I . The precise Lamb-dip frequencies were analyzed together with new Doppler-limited measurements including lines in excited vibrational states (up to $v=3$) and data taken from the literature. A global fit yielded a new set of isotopically invariant parameters. The hyperfine interactions of the ^{13}C and ^{17}O isotopomers were also included in the global analysis. The new set of molecular parameters provides highly accurate frequency predictions of lines in the THz-range for the pure rotational spectrum of all CO isotopomers.

COLLISION-INDUCED ABSORPTION BANDSHAPES IN O₂ AND CO₂: INTERPLAY OF LINE-MIXING EFFECT AND VAN DER WAALS ASSOCIATION

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Collision-induced absorption (CIA) spectra in the regions of the oxygen fundamental ^a and the carbon dioxide Fermi doublet ^b are remeasured recently at high resolution using FTIR technique. Notable fine structure is detected in both cases, the attribution of which can throw a new light on the nature of the underlying spectroscopic phenomenon as well as on the general properties of intermolecular interactions. This concerns also a variety of atmospheric and astrophysical applications.

In case of oxygen this fine structure manifests itself particularly as weak regular ripples out-of-phase respective to ro-vibrational lines permitted by selection rules. Also in oxygen and more clearly in carbon dioxide spectra *P, Q, R*-like structure is seen on top of smooth CIA background. Present work shows these spectroscopic fine structures to be due to interplay of line-mixing effect and Van der Waals association. The former causes seeming distortion of the ro-vibrational structure, the latter is responsible for the symmetric-top-like structure in a spectrum of weakly bound dimers which stands out from the smooth background near the band center.

Spectral simulation of the dimeric features in CIA spectra of carbon dioxide allows for determination of the effective thermally averaged rotational constants $A = 0.33 \text{ cm}^{-1}$ and $\tilde{B} = 0.034 \text{ cm}^{-1}$. These are notably at variance to the ground state values $A = 0.3 \text{ cm}^{-1}$ and $\tilde{B} = 0.049 \text{ cm}^{-1}$. For the oxygen dimer the value of $\tilde{B} = 0.038 \text{ cm}^{-1}$ has been found. The changes in rotational constants are indicative of significant distortion of the dimer ground state geometry upon thermal excitation.

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ARE FREQUENCY LINESHIFTS ADDITIVE ? THE AMMONIA SPECTRUM AS AN EXPERIMENTAL TEST OF THE RYDBERG-RITZ PRINCIPLE

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The Rydberg-Ritz combination principle is frequently invoked to give a physical support to the frequency additivity rule inside a level manifold. Rigorously, this principle applies only in the absence of relaxation^a and its failure was recognised by the consideration of pressure induced frequency lineshifts reported on a limited number of NH₃ transitions.^b Recently,^c it was stressed that the consequences of this failure can be observed on pressure induced lineshifts and line broadenings as well.

In order to get a better insight in this feature, the low J and K level manifold of the ground and ν_2 states of NH₃ has been considered. In this purpose, pressure induced frequency lineshifts, as well as a limited number of pressure induced line broadenings, were systematically measured for the ν_2 band, and combined with other previously published results for the inversion and rotational lines of NH₃.

Dealing with pressure induced lineshifts, statistical tests allow to obtain a quite meaningful experimental evidence that the Rydberg-Ritz principle fails in the presence of relaxation, that is pressure induced frequency lineshifts are not additive.^d With regards to line broadenings, it is shown that a significant experimental evidence of this failure calls for new and more precise line broadening measurements.

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^cS. Belli, G. Buffa, O. Tarrini, *Chem. Phys. Lett.* **271**, 349-354 (1997).

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AIR-BROADENING AND SHIFT COEFFICIENTS AND LINE MIXING IN THE ν_3 , ν_5 , AND ν_6 BANDS OF $^{12}\text{CH}_3\text{D}$

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A multispectrum nonlinear least squares fitting technique^a has been used to determine Lorentz air-broadening coefficients and air-induced shift coefficients for transitions in the ν_3 , ν_5 , and ν_6 fundamental bands of $^{12}\text{CH}_3\text{D}$ in the spectral region between 1150 and 1600 cm^{-1} . Eleven high-resolution (0.005 cm^{-1}) room-temperature absorption spectra, recorded using the 1-m Fourier transform spectrometer (FTS) at the McMath-Pierce facility of the National Solar Observatory at Kitt Peak, were simultaneously analyzed. The data set included both low-pressure (1 to 3 Torr) spectra of 98% pure CH_3D and spectra of lean mixtures ($\approx 1\%$) of CH_3D in dry air at total pressures from about 100 Torr to 400 Torr. Cell path lengths of 25 and 150 cm were used.

Air-broadening coefficients were determined for more than 360 ν_3 transitions^b, 400 ν_5 transitions^c, and 670 transitions in the ν_6 band^d. These results include transitions with rotational quantum numbers as high as $J'' = 17$ and $K'' = 17$ and, in the two perpendicular bands (ν_5 and ν_6), 46 forbidden transitions with $2 \leq |\Delta K| \leq 4$. Air-induced shift coefficients were also determined for most of the transitions analyzed. The measured broadening coefficients range from 0.016 to 0.076 $\text{cm}^{-1} \text{atm}^{-1}$ at 296K, and the shift coefficients vary from about -0.012 to +0.008 $\text{cm}^{-1} \text{atm}^{-1}$. The majority of the shifts are negative. The $J'' = K''$ transitions in the $^P P$, $^Q Q$, and $^R R$ sub-bands are associated with the smallest broadening coefficients. Weak line mixing effects have been observed in some high- J transitions with $K'' = 3$ in all three bands, and we have determined off-diagonal relaxation matrix element coefficients for their $A^+ A^- (A_1 A_2)$ split components. Variations of the measured parameters with vibrational and rotational quantum numbers and transition symmetry species will be discussed. We will also compare our measurements with the values on the current HITRAN compilation^e and with other available measurements.

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LINE MIXING IN WATER VAPOR SPECTRUM:
NON-LINEAR PRESSURE SHIFTS IN THE $\nu_2 + \nu_3$ BAND

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The water vapor spectra between 5000 and 6000 cm^{-1} broadened by N_2 , O_2 and He pressures were measured using the FT-spectrometers of NIST, USA at buffer gas pressures from 148.5 to 3800 Torr. The measurements were made for lines of (011)-(000) band with spectral resolution of 0.007 cm^{-1} . The Voigt contour was used to determine line positions, halfwidths and strengths. The clear nonlinear pressure dependencies of the line positions were found for the case of $H_2O - He$ collisions. For the cases of $H_2O - N_2$ and $H_2O - O_2$ collisions the shift is mostly linear on pressure, but for several closely spaced lines the non-linear dependencies of the line shifts were revealed. The theoretical analysis was made using formulas developed recently by Thibault, Boissoles, Le Doucen et al ^a taking into account the line mixing effects within the perturbation approach. The non-diagonal elements of relaxation matrix were calculated using the formulas given by Cherkasov^b, only the leading dipole-quadrupole interaction was taken into account for the cases of $H_2O - N_2$ and $H_2O - O_2$ collisions, whereas the dispersion and induction interactions were included for the case of $H_2O - He$ collisions. The calculations have shown that the line mixing gives negligible contribution into the shift for most of lines for $H_2O - N_2$ and $H_2O - O_2$ systems, but it was found that in the cases of 7 3 5 - 6 3 4 (line center - 5507.526 cm^{-1}) and 8 1 7 - 7 1 6 (line center - 5507.828 cm^{-1}) transitions of the $\nu_2 + \nu_3$ band the line interference can give the essential addition to the total line shift leading to the nonlinear dependence on the perturber gas pressure. The non-linear behavior of line shift is more evident for the $H_2O - He$ collisions. The calculated non-linear shift coefficients are in qualitative agreement with measured ones. The authors acknowledge the support by the Russian Foundation of Fundamental Research (Grant N 98-02-16375 and N 98-02-17772).

^aF.Thibault Profils spectraux et collisions moléculaires These de docteur en sciences, IÜ universite Paris XI Orsay (1992)

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**HIGH RESOLUTION FTIR INVESTIGATION ON THE
1,3,5-TRIAZINE ISOTOPOMER $C_3^{15}N_3D_3$**

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The FTIR spectra of the 1,3,5-triazine isotopomer $C_3^{15}N_3D_3$ (MS group D_{3h}) have been recorded with a resolution of about 0.002 cm^{-1} . The parallel bands ν_{11} and ν_{12} and the perpendicular bands ν_9 and ν_{10} have been assigned and analysed. The ground state constants and the constants of the states $\nu_9 = 1$, $\nu_{10} = 1$, $\nu_{11} = 1$ and $\nu_{12} = 1$ up to the H's will be presented and discussed.

LINE POSITIONS OF PHOSPHINE IN THE 3 μm REGION FOR PLANETARY SPECTRA ANALYSIS

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A preliminary study of the high resolution spectrum of phosphine PH_3 in the 3 μm region between 3000 to 3600 cm^{-1} is reported. The objective is to provide a prediction for planetary spectra studies because the absorption of the Saturnian atmosphere in this spectral interval is essentially due to phosphine. No analysis of this region has been attempted previously. For this, 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, some 250 lines have been assigned up to $J=8$ in the $\nu_1+\nu_2$, $\nu_3+\nu_4$, $\nu_1+\nu_4$ and $\nu_2+2\nu_4$ centered around 3307, 3425, 3432 and 3215 cm^{-1} respectively. Other bands expected to contribute absorption in this region are $\nu_2+\nu_3$ and the overtone $3\nu_4$ near 3319 cm^{-1} and 3354 cm^{-1} respectively. As in the 5 μm region ^a where 5 vibrational states were interacting, we anticipate that different Coriolis and Fermi-type interactions to couple all the unknown states in the 3 μm region. ^b

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^bPart 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.

**FAST SCAN SUBMILLIMETER SPECTROSCOPIC
TECHNIQUE (FASSST): SPECTROSCOPIC AND
ANALYTICAL APPLICATIONS**

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The Fast Scan Submillimeter Spectroscopic Technique (FASSST)^a, based on voltage tunable Backward Wave Oscillators (BWOs) and optical calibration methods, has been successfully extended to the lower end of the submillimeter wave spectrum. FASSST now provides continuous submillimeter wave spectra from 120–650 GHz in a short time. Examples of interesting spectra will be presented.

Due its speed, FASSST is an excellent tool for recording the spectra of unstable molecules and of pyrolysis products. In addition, FASSST has been successfully used to identify gas components in gas mixtures^b. This will be demonstrated using the spectra of a mixture of SO₂, cyclopentene oxide and trimethyl sulfane.

^aD.T. Petkie, T.M. Goyette, R. Bettens, S.P. Belov, S. Albert, P. Helminger and F.C. De Lucia, *Rev. Sci. Instrum.*, **68**, 1675–1683 (1997).

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DIFFERENTIAL UV SPECTROSCOPIC STUDIES OF Ag^+ INTERACTION WITH NATURAL DNA AND NUCLEOTIDES

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In addition to their antibacterial effect, Ag^+ ions are noted for mutagenic and carcinogenic activity which attracts much interest to Ag^+ complexes with natural polynucleotides and their monomers.

UV differential spectroscopy was applied to study the interaction of Ag^+ ions with ribo- and deoxyribonucleotides of canonical bases (GMP, dGMP, AMP, dAMP, CMP, dCMP, UMP, dTMP) and native DNA. Heteroatoms of the bases, coordinating ions, and binding constants which characterize the formation of metal complexes were found. The ion influence on the parameters of the DNA helix-coil transition was estimated.

Ag^+ ions binding to N7 and O6 of individual dGMPs causes deprotonation of N1 upon dimer formation. In DNA this interaction (a "strong" complex) results in internal protonation of cytosine due to a proton transfer from N1G to N3C in GC-pairs, which follows directly from the shape of differential UV spectrum. A "strong" complex formation is accompanied by increase in DNA thermal stability and by change in its melting interval.

Ag^+ ions form "weak" complexes with GC- and AT-pairs of DNA also. The complexes are supposed to be linear chelates N3C- Ag^+ -N7G and N3T- Ag^+ -N7A. Such chelates are formed due to the purine transition from anti- to syn-conformation. The positive cooperativity of the Ag^+ -DNA binding during the formation of a "weak" complex is dictated by the cooperativity of the DNA transition into the new double-helical conformation. The complex stability is too high: at $[Ag^+]/P$ more than 0,16 (P and $[Ag^+]$ are concentrations of phosphorus of DNA and Ag^+ respectively) DNA does not melt up to 96° C.

COMPETITION BETWEEN ORBITAL ANGULAR
MOMENTUM AND VIBRATIONAL RESONANCE EFFECTS
IN THE SPECTRUM OF NH₂

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The $\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1$ electronic transition of the NH₂ free radical is one of those best characterised experimentally. It has been known since the pioneering work of Jungen, Hallin and Merer.^a that it provides an excellent vehicle for studying the interplay between orbital angular momentum effects and vibrational resonances. We have extended the stretch-bender calculation of Duxbury et. al. ^bto include the effects of overall rotation and spin-rotation interaction. The suite of computer programs based on this theoretical model is used to calculate the ro-vibronic structure for a range of vibronic states of NH₂, including those in which K_a is very large. The results of these calculations are compared with those recently published using the Carter-Handy-Rosmus method ^cwith optogalvanic and Fourier transform measurements of I. Hadj-Bachir et al.^d and also with recent time resolved fluorescence measurements made by Reid and Loomis at JILA .^e

^aCh. Jungen, K.-E. J. Hallin and A. J. Merer, *Molec. Phys.* **40**, 25 (1980)

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^dI. Hadj-Bachir, T. R. Huet, J-L. Destombes and M. Vervloet, *J. Mol. Spectrosc.*, **193**, 326 (1999)

^eJ. P. Reid, R. A. Loomis and S. R. Leone, *J. A. C. S. Abstr.* **217**, 169 (1999)

**SPECTROSCOPY IN THE VUV RANGE
AT A RESOLUTION OF 0.01 cm^{-1}**

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A new broadly tunable (12-17 eV) high resolution VUV laser system is presented. This system enables the recording of photoabsorption, photoionisation, and photoelectron spectra at high resolution. The bandwidth of 0.01 cm^{-1} opens new prospect for VUV photo chemistry and photophysics.

This work is supported financially by ETH Zürich and the Swiss National Foundation.

ANALYSIS OF THE FOURIER TRANSFORM EMISSION SPECTRA OF NH₂ IN THE 6 000–10 000 cm⁻¹ REGION

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Fourier transform emission spectra of NH₂ recorded with a Bomem spectrometer have been investigated in the 6 000–10 000 cm⁻¹ region. Using the rotational energy levels of Vervloet,^a McKellar *et al.*,^b and Bachir *et al.*^c about 2 000 transitions could first be assigned and connect states of the type $(0v'_2 0)\tilde{A}$ and $(0v''_2 0)\tilde{X}$ states, with $v'_2 = 0, 1, \text{ or } 2$ and $v''_2 = 1, 2, 3, 4, \text{ or } 5$ (using bent molecule notation for both states). Transitions involving rotational levels for which no data were available^{a,b,c} could afterwards be identified and this provided us with information on some of the least well known vibrational states of the \tilde{X} electronic state, such as the (030), (040), or (050) states. All the assigned transitions were used as input for a least-squares fit analysis which made it possible to obtain the energy of the rotational levels involved as well as its uncertainty. For some rotational levels of the (030), (040), or (050) vibrational states belonging to the \tilde{X} electronic states, the first determination of their energy was carried out. At last, all the available levels were fitted in order to retrieve accurate bending mode potential energy functions for both the \tilde{X} and \tilde{A} electronic states. These functions compare favorably with those obtained by Dixon *et al.*^d

^aM. VERVLOET, *Molec. Phys.* **63**, 433–449 (1988).

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THE ν_1 AND ν_2 BANDS OF AR-HN₂⁺: AN EXAMPLE OF AN EXCEPTIONAL VIBRATIONAL ANHARMONICITY

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A combined theoretical and experimental study of the ν_1 and ν_2 stretching vibrations of Ar·HN₂⁺ is presented. These correlate asymptotically with the NH and NN stretching vibration of HN₂⁺, respectively, but undergo exceptionally strong anharmonic interaction with each other in the complex. As a consequence, the ν_2 band experiences an unusually large anharmonicity contribution to the red shift and a dramatic increase in intensity. The first observation of this band by means of tunable diode laser absorption spectroscopy in a supersonic slit nozzle plasma is reported. The band origin is found at 2041.1802(3) cm⁻¹. The ν_1 band origin is located at 2505.5000(2) cm⁻¹ and a ground state rotational constant of 0.080868(6) cm⁻¹ has been determined.

MILLIMETER WAVE INTRACAVITY JET SPECTROMETER FOR STUDY OF WEAKLY BOUND MOLECULAR COMPLEXES

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An extremely sensitive intracavity millimeter wave spectrometer with a pulsed supersonic jet has been constructed for the investigation of weakly bound van der Waals (vdW) complexes.

The spectrometer utilizes an OROTRON oscillator as the tunable, coherent source of radiation from 107 - 145 GHz. The key feature of this technique is that the molecular jet expands into the high quality resonator of the OROTRON and the absorption inside the cavity is detected by the variation of the electron current of the OROTRON in the collector circuit. The spectrometer provides sub-Doppler spectral resolution without any phase or frequency stabilization. The new spectrometer has been adjusted and tested by measuring the $J = 1 - 0$ transition of CO and some of its rare isotopomers in natural abundance. The improvement of sensitivity for more than two orders of magnitude of OROTRON spectrometer was achieved in comparison with the existing single path schemes.

The spectrometer has been used in order to investigate the spectra of different vdW complexes, which are made of astrophysically important atoms and molecules, such as He, Ne, Ar, H₂, D₂, N₂, CO. The obtained results on spectroscopy of CO-Ar, CO-Ne, CO-N₂, CO-*para*H₂, CO-*ortho*D₂, CO-He will be presented.

**ROTORSIONAL SPECTRA
OF $(CH_3)_3X - Y$ TYPE MOLECULES**

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Rotational transitions of compounds containing a $(CH_3)_3X$ group are split into a number of torsional lines due to methyl internal rotation. The width of the multiplet is determined by the torsional barrier and increases with the size of the X atom. Generally, the fine structure is rather narrow and high resolution molecular beam FT microwave spectrometers are needed to resolve it. This and computational problems, made such internal motions only recently available for spectroscopic investigations.

We recorded the rotational spectra of several isotopomers of $(CH_3)_3SiCN$, $(CH_3)_3SiCl$, $(CH_3)_3SiBr$, and $(CH_3)_3GeCl$ in the microwave and millimeter wave region. It has been possible to determine the heavy atom structure of these molecules. Moreover, quadrupole coupling of the $^{35/37}Cl$, $^{79/81}Br$, and ^{14}N nuclei have been investigated. Barriers to internal rotation have been determined from well resolved low J transitions.

Changes in the molecular structure and the barrier to internal rotation for the different substituents $Y = CN, Cl$, and Br as well as the influence of the center atom $X = C, Si, Ge$ will be discussed. Also computational and group theoretical considerations will be presented.

MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF VINYLSTIBINE

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The vinylstibine (CH_2CSbH_2) is synthesized in a two step sequence : the reaction of vinyltributylstannane with antimony trichloride gives the vinyl-dichlorostibine. The chemoselective reduction with Bu_3SnH in the presence of small amounts of a radical inhibitor gives the vinylstibine in a 60% yield. Photoelectronic spectra have already been published^a.

Vinylstibine is an isoelectronic compound of vinylamine, vinylphosphine and vinylarsine (three molecules formerly studied in our lab). The length of the C-Sb bond compared to alkyls, the role of the Sb atom and the interaction "double bond – free doublet" have motivated the microwave study of vinylstibine.

Vinylstibine presents mainly 2 isotopomers : 57% of ^{121}Sb with a spin 5/2 and 43% of ^{123}Sb with a spin 7/2 leading to a rather complicated overlapped spectrum.

Using our Microwave Fourier Transform Spectrometer ^b we have recorded the rotational spectrum of four species in natural abundance : $^{121}\text{Sb}^{12}\text{C}$, $^{123}\text{Sb}^{12}\text{C}$, $^{121}\text{Sb}^{13}\text{C}$, $^{123}\text{Sb}^{13}\text{C}$, where the substituted C is the C linked to Sb.

We have determined both the rotational constants and part of the Sb quadrupole coupling tensor for the four species.

The rotational constants confirm the structure obtained with SCF level ab initio calculations. We will compare the C-Sb bond length in vinylstibine to C-N in vinylamine^c C-P in vinylphosphine^d and C-As in vinylarsine^e.

^aS. Legoupy, L. Lassalle, J.C. Guillemin, V. Metall, A. Senio, G. Pfister-Guillouzo, *Inorg. Chem.* **35**, 1466 (1995).

^bS. Kassi, D. Petitprez, G. Wlodarczak, *J. Mol. Struct.*, to be published

^cF.J. Lovas, F.O. Clark and E. Tiemann, *J. Chem. Phys.* **62**, 1925-1931 (1975).

^dP. Dréan, M. Le Guennec, J.C. López, J.L. Alonso, J.M. Denis, M. Kreglewski and J. Demaison, *J. Mol. Spectrosc.* **166**, 210-233 (1994).

^eP. Dréan, D. Petitprez, J. Demaison, J.C. López, J.L. Alonso, J.C. Guillemin, and J.E. Boggs, *J. Mol. Spectrosc.* **190**, 365-371 (1998).

A NONADIABATIC FRANCK-CONDON CALCULATION OF THE $\tilde{A}^2B_2 \leftarrow \tilde{X}^2A_1$ ABSORPTION SPECTRUM OF NO_2

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Using available functional forms for the diabatic potential energy surfaces and the non-diagonal coupling term,

- LPHB diabatic potential energy surface for the excited state and coupling term^a, modified by Salzgeber et al.^b
- Diabatic surface extracted from the SPJT effective potential energy surface for the fundamental state^c,

the $\tilde{A}^2B_2 \leftarrow \tilde{X}^2A_1$ absorption spectrum of NO_2 is computed, expanding the Hamiltonian matrix on the diabatic basis-set of the two electronic states. The 2B_2 and 2A_1 components of the wavefunctions of the excited vibronic states are analysed. The calculated transition frequencies and Franck-Condon intensities are compared with the experimental spectrum. A low resolution calculation from the fundamental level is shown to follow satisfactorily the observed features.

^aE. Leonardi, C. Petrongolo, G.Hirsch and R.J. Buenker, *J. Chem. Phys.*, **105** (20), 9051 (1996)

^bR.F. Salzgeber, V. Mandelshtam, Ch. Schlier, H.S. Taylor, *J. Chem. Phys.*, **109**(3), 937 (1998)

^cJ.H. Schryber, O.L. Polyansky, P. Jensen and J. Tennyson, *J. Mol. Spectr.*, **185**, 234 (1997)

THE DENSITY MATRIX OF H₂O - N₂ IN THE COORDINATE REPRESENTATION: A MONTE CARLO CALCULATION OF THE FAR-WING LINE SHAPE

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Within the formalism developed previously for the calculation of the far-wing line shape for molecular systems, the complete set in Hilbert space is constructed from the eigenfunctions of the unperturbed Hamiltonians of the absorber and bath molecules. As a result, one has to spend most of the computer resources to diagonalize the anisotropic potential matrix whose size is determined by the number of states included. For systems of interest in atmospheric applications, this limited the number of states that could be included and the accuracy attainable. Recently, a new formalism has been developed in which the eigenfunctions of the orientations of the system are chosen as the complete set. The advantage of this coordinate representation is that the diagonalization procedure becomes unnecessary and the commutativity of the anisotropic potential and the dipole moment always remains valid because all operators depending on the coordinate variables only are diagonal. Meanwhile, as many states as desired can be included in the calculation of the density matrix which becomes off-diagonal. The main computational task is to carry out multidimensional integrations over the continuous variables which specify the initial and final orientations of the systems during transition processes. For systems consisting of linear molecules such as CO₂ - CO₂, the dimension of integrations is 7 and we have shown that one is able to evaluate them^{a,b}. For more complicated systems involving asymmetric-top (or symmetric-top) molecules such as H₂O - N₂ and H₂O - H₂O, the dimensionality is 9 and 11, respectively. At the present time, it is difficult to evaluate these integrations using standard methods, and one has to make an additional assumption about the form of the potentials considered in order to make the problem tractable. However, the Monte Carlo method can be used, at least in the H₂O - N₂ case, to evaluate the 9-dimensional integrations. Therefore, introducing the density matrix in the coordinate representation and using the Monte Carlo method, one is able to obtain the far-wing line shapes for H₂O - N₂ without making any simplifying assumptions. Results will be presented and compared with experiment.

^aQ. Ma and R. H. Tipping, *J. Chem. Phys.* **108**, 3386 (1998).

^bQ. Ma, R. H. Tipping, C. Boulet and J. -P. Bouanich, *Appl. Optics* **38**, 599 (1999).

**INFRARED SPECTROSCOPY ON THE LOWEST TRIPLET
STATE OF THE PYRAZINE-ARGON COMPLEX USING A
FREE ELECTRON LASER**

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Mass-selective gas-phase infrared spectroscopy is used to measure the infrared spectrum of the lowest triplet state of the pyrazine-argon complex. As an infrared excitation source a free electron laser is used. A tunable dye laser is used to excite the vibrationless $T_1 \leftarrow S_0$ transition of the pyrazine-argon complex, the origin of which is found to be 16.6 cm^{-1} red-shifted from the $T_1 \leftarrow S_0$ transition of pyrazine (26820 cm^{-1} ^a). A second dye laser, tuned just above the IP, subsequently ionizes the complex. The free electron laser, fired in between the two dye lasers, is used to excite vibrations in the triplet state of the pyrazine-argon complex, after which the cluster dissociates. The infrared spectrum of the pyrazine-argon complex is thus measured by monitoring the depletion of the pyrazine-argon ion signal as a function of the infrared wavelength.

With this technique the infrared spectrum of the triplet state of the pyrazine-argon complex could be measured in the $200\text{-}2000 \text{ cm}^{-1}$ range. This spectrum is strongly distorted by vibronic coupling with higher lying singlet and triplet states.

^aS. Kobayashi, K. Kikuchi, and H. Kokubun, Chem. Phys. **27** (1978) 399

ANALYTICAL APPROXIMATION FOR ADIABATIC CORRECTION, NONADIABATIC MATRIX ELEMENTS AND TRANSITION MOMENTS OF RYDBERG DIATOMIC STATES IN QUANTUM DEFECT THEORY. APPLICATION TO $s, d^3\Sigma_g^+$ STATES OF HYDROGEN MOLECULE

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Multi-channel quantum defect theory (MQDT) is applied to approximate the Born-Oppenheimer (BO) Rydberg diatomic states. The BO electronic wavefunctions (WFs) represented as a linear combination of the one-channel diabatic WFs are obtained by a diagonalization of the so-called MQDT reaction matrix which takes into account electronic interaction between the various channel motion of the remote electron. The method requires knowledge only of the BO potential curves for the lowest members of the Rydberg series plus the adiabatic potentials for ground and first excited states of the positive ion. Closed expressions for the adiabatic and nonadiabatic matrix elements for coupling between any electronic states belonging to the same Rydberg series are derived by a combination of analytical differentiation of the multi-channel BO WFs with respect of internuclear distance R and previous results developed in one-channel QDT approximation ^a. The molecular transition dipole moments as a parametric function of R are evaluated using the MQDT WFs representation and the quantum-mechanical and semiclassical approaches to the calculation of radial integrals between one-channel QDT functions ^b. The theory is tested by a calculation of adiabatic correction, nonadiabatic matrix elements and transition moments of the hydrogen molecule corresponding to the triplet Rydberg states with $n = 2 - 4$. For small and intermediate internuclear distance the agreement with high-accurate *ab initio* data is found to generally good, and in some cases identical results are obtained.

^aA.V.STOLYAROV, V.I.PUPYSHEV AND M.S.CHILD, Analytical approximations for adiabatic and non-adiabatic matrix elements of homonuclear diatomic Rydberg states. Application to the singlet p-complex of the hydrogen molecule *J.Phys.B.***30**, 3077-3093 (1997).

^bA.V.STOLYAROV AND M.S.CHILD, Radiative properties of diatomic Rydberg states in quantum defect theory. Application to the hydrogen molecule *J.Phys.B.***32**, 527-535 (1999).

MOLECULAR ANHARMONICITY - A COMPUTER AIDED TREATMENT

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We present a new software package for the theoretical treatment of anharmonic vibrational spectra of non-linear polyatomic molecules. The package, called "B&D" [1], computes vibrational energies starting from sets of force constants defined as potential energy derivatives. The method employed [2-5] allows us to combine experimental rotation-vibration data with any information made available from *ab-initio* calculations. The package follows the natural procedure in which a molecular problem is solved, both in the symbolic construction of Hamiltonian operator and basis functions and in the numerical computation of the Hamiltonian matrix elements.

The approach includes an expansion of the Hamiltonian in a power series of the internal coordinates, its transformation to symmetry coordinates, the evaluation of the Hamiltonian in a matrix form with a basis of harmonic oscillator wavefunctions in symmetry coordinates, the transformation of this matrix to a symmetry adapted basis, and the diagonalization of the transformed matrix.

The novelty consists in making the entire procedure fully automatic, so that the occurrence of errors is greatly reduced and the laborious process involved in deriving and implementing the Hamiltonian is dramatically simplified.

[1] R. G. Della Valle, L. Halonen and E. Venuti,

B&D User's Manual, <http://www.chim.unifi.it:8080/~valle/>.

[2] T. Lukka, E. Kauppi and L. Halonen, *J. Chem. Phys.* **102**, 5200 (1995).

[3] E. Kauppi and L. Halonen, *J. Chem. Phys.* **103**, 6861 (1995).

[4] L. Halonen, *J. Chem. Phys.* **106**, 831 (1997).

[5] E. Venuti, L. Halonen and R. G. Della Valle, *J. Chem. Phys.* **110**, 7339 (1999).

Invited Lectures C

Monday, September 6, 14:00

Chairman : J.-P. CHAMPION

REDUCTIONS—A WAY HOW TO DETERMINE UNAMBIGUOUS SPECTROSCOPIC CONSTANTS WITH A CLEAR PHYSICAL MEANING

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The parameters of the effective Hamiltonian—spectroscopic constants containing information on the structure and force field of a molecule are determined by fitting the experimental data. Quite often the problems are encountered in the process that can be attributed to two classes of causes

- **Shortage of data.** In simple terms it means that we are trying to determine more parameters than our data would allow and the required information on some, usually higher-order parameters, simply is not there.
- **Collinearities.** Another source of the problem may be the collinearity which means that the following equation is satisfied for all values of j

$$c_1 \frac{\partial y_j}{\partial x_1} + c_2 \frac{\partial y_j}{\partial x_2} + \dots + c_p \frac{\partial y_j}{\partial x_p} = 0, \quad (1)$$

where x_i are the parameters to be determined by fitting the data y_j and c_i are constants. When such problem occurs it is often treated by constraining one of the parameters in the fit. The constraint solves the problem, because one term disappears from Eq.(1), but it is not clear how the remaining parameters in the fit are affected and their physical meaning is obscured.

The origin of collinearities (1) has been explained by Watson^a who has shown that the observed indeterminacies were caused by existence of a transformation which transforms the values of parameters – spectroscopic constants x_i ($i = 1 \dots m$) – in the effective Hamiltonian H

$$\tilde{x}_i = x_i + f_i(x_1, \dots, x_m; s_1, \dots, s_p). \quad (2)$$

without changing its eigenvalues. The indeterminacy problem is caused by free parameters s_k , each s_k is the source of one collinearity (1) and the problem can be solved by constraining p molecular parameters \tilde{x}_i , p being the number of the free parameters s_i . These constraints together with Eq.(2) assign the definite

^aJ. K. G. Watson *Vibrational Spectra and Structure* (J. Durig, Ed.), Vol.6, pp. 1-89, Elsevier, Amsterdam, 1977.

values to all s_i and when these are substituted to Eq.(2) for the unconstrained parameters they give the clear physical meaning to the parameters retained in the fit.

The procedure described is usually called a reduction. The reduction method provides the answers to the very practical questions related to spectroscopic data fitting, namely: how many constraints are to be applied and which parameters should be constrained? If such constraints are applied, what is the physical meaning of the remaining parameters? A few examples of successful applications will be presented. The numerous applications of the reductions demonstrated repeatedly that they are an appropriate solution for the indeterminacy problems^b.

^bK. Sarka, D. Papoušek, J. Demaison, H. Mäder and H. Harder *Vibration-Rotational Spectroscopy and Molecular Dynamics, Advanced Series in Physical Chemistry* (D. Papoušek, Ed.), Vol.9, pp. 116-238, World Scientific, Singapore, 1997.

GLOBAL ROVIBRATIONAL ANALYSIS OF LINEAR MOLECULES

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Such an analysis concerns the rovibrational energies in the electronic ground state of a given isotopomer of a linear molecule. The main goal is to reproduce all available experimental data [microwave, (sub-)millimeter wave, RF, infrared (mainly F.T.), and laser spectra] in agreement with their experimental uncertainty. To reproduce the data even in the numerous cases of strong interactions, we develop a model with as few off-diagonal terms as possible (generally the rotational and the vibrational l-type resonance and a few anharmonic resonance terms). For each J value of interest, we construct energy matrices where all those off-diagonal terms of our Hamiltonian are taken into account simultaneously. According to a classical weighted least-squares procedure, we so obtain a set of about 100 to 150 molecular parameters from which we can calculate any rovibrational level with a good accuracy thanks to the coherence of the analysis.

The first global analysis of a linear molecule has been performed thirty years ago by Josef Pliva on the nitrous oxide molecule N_2O ^a. We have developed the same kind of analysis for the carbonyl sulfide molecule OCS and its isotopic varieties, and this analysis has been applied to some other triatomic molecules: $^{35}ClCN$, $^{37}ClCN$, FCN, and $^{16}O^{12}C^{80}Se$. In the nineties, we have developed new programs to perform global analyses of linear pentatomic molecules, with application to HCCCN, DCCCN and HCCNC molecules.

On the basis of examples about those molecules, many aspects of the global analyses will be discussed: the model, the experimental data and their weights, the correlations between the parameters, the constraints applied to the parameters, the use of ab-initio values, the stability of the convergence of the least-squares process, the calculation of the state parameters, the labeling of the heavily mixed states, the calculation of intensities on the basis of the eigenvectors, the extension to the rare isotopomers, and the calculation of energies under a Stark field. The application to linear molecules with 4, 6 or 7 atoms will also be discussed.

^aJ. Mol. Spectrosc. 27, 461-488 (1968).

Poster Session D
Monday, September 6, 16:00

GLOBAL ROVIBRATIONAL ANALYSIS OF HCCNC BASED ON NEW INFRARED AND SUBMILLIMETER-WAVE SPECTRA

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Isocyanacetylene (HCCNC), synthesized for the first time in 1991^a, has been detected in the interstellar cloud TMC-1^b, and more recently in the star IRC+10216^c. It has been investigated by millimeter-wave spectroscopy^d in the lowest excited vibrational states, and by Fourier transform infrared spectroscopy^e. Many lines in the recorded spectra remained unexplained due to the high density of states and the numerous interactions between them, giving rise to many local perturbations. We have applied a global rovibrational analysis to those infrared and millimeter-wave spectra and a good statistical agreement has been obtained. In our model, we have considered the rotational and vibrational ℓ -type resonances and the most important anharmonic resonances. This work will be published shortly.

New spectra have been recently recorded both in the infrared and millimeter-wave domains, using new material. The precursor, pentacarbonyl(1,2-dichlorovinylisocyanide)chromium $[(CO)_5Cr(CNCCl = CHCl)]$, was synthesized in Berlin according to the method of Fehlhammer and Beck^f. HCCNC was obtained from this chromium complex by vacuum pyrolysis at 240°C. The new rotational spectra were recorded in Kiel in the ranges 40 to 120 GHz, 240 to 340 GHz, and 340 to 520 GHz. On the basis of predictions generated by the global analysis, more than 1200 lines have been measured with a typical

^aM. Krüger, H. Dreizler, D. Preugschat, and D. Lentz, *Angew. Chem. Int. Ed. Engl.* **30**, 1644-1646 (1991)

^bK. Kawaguchi, M. Ohishi, S. Ishikawa, and N. Kaifu, *Astrophys. J.* **386**, L51-L53 (1992)

^cP.D. Gensheimer, *Astrophys. J.* **479**, L75-L78 (1997)

^dA. Guarnieri, R. Hinze, M. Krüger, and H. Zerbe-Foese, *J. Mol. Spectrosc.* **156**, 39-47 (1992)

^eH. Bürger, S. Sommer, D. Lentz, and D. Preugschat, *J. Mol. Spectrosc.* **156**, 360-372 (1992)

^fW. P. Fehlhammer, G. Beck, *J. Organomet. Chem.* **379**, 97-106 (1989)

accuracy of 15 to 25 kHz. They mostly concern vibrational states up to 1500 cm^{-1} . As the previous measurements were limited to 150 GHz for most states, these new measurements yield fundamental informations about the numerous interactions between those states.

The new infrared measurements have been recorded in Wuppertal, with experimental conditions considerably better than for the previous measurements. The bands ν_5 , $2\nu_5$, $\nu_6 + \nu_7$, ν_4 , and $2\nu_6$ are measured with a better accuracy, up to higher J values, and new hot bands could be identified. Below 500 cm^{-1} , the ν_7 and $2\nu_7$ bands have been recorded for the first time.

All those new measurements have been included in the global fit of which detailed results will be given.

GLOBAL FITTINGS OF ROVIBRATIONAL LINE POSITIONS OF NITROUS OXIDE

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The effective operator approach has been applied to the global fitting of vibrational-rotational line positions of $^{14}\text{N}_2^{16}\text{O}$. For this purpose the effective Hamiltonian derived by Teffo and Chedin^a has been extended up to sixth order in the Amat-Nielsen ordering scheme. The reduction of this effective Hamiltonian by means of unitary transformations has been performed. About 140 parameters of the reduced effective Hamiltonian have been fitted to 18000 observed line positions collected from the literature. An RMS deviation of 0.0025 cm^{-1} has been achieved in the fitting. The predictive abilities of the obtained set of parameters have been analyzed.

^aJ.-L. Teffo and A. Chedin *J. Mol. Spectrosc.* **135**, 389-409 (1989).

THE $2\nu_1 + 5\nu_3$ TRIADS OF $^{12}\text{C}^{16}\text{O}_2$ AND $^{13}\text{C}^{16}\text{O}_2$: OVERTONE SPECTROSCOPY AND COMPARISON WITH A GLOBAL ANALYSIS OF THE VIBRATION - ROTATION STRUCTURE

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The $2\nu_1 + 5\nu_3$ triad of carbon dioxide has been investigated for the first time at high resolution, by means of overtone spectroscopy in the visible region. Among the three vibrational states of Σ_u^+ symmetry ($2\ 0^0\ 5$, $1\ 2^0\ 5$, $0\ 4^0\ 5$, labeled 20051, 20052, 20053 in HITRAN notation), the two first ones have been evidenced for $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$. The $2\ 0^0\ 5 - 0\ 0^0\ 0$ and $1\ 2^0\ 5 - 0\ 0^0\ 0$ overtone bands have been recorded by Intracavity Laser Absorption Spectroscopy (ICLAS) and Photoacoustic Spectroscopy (PAS) respectively, using a Titanium Sapphire laser, and with a typical sensitivity of a few $10^{-9}\ \text{cm}^{-1}$.

For $^{12}\text{C}^{16}\text{O}_2$ a cell pressurized at about 260 Torr was inserted into the cavity of an ICLAS spectrometer at Grenoble. The spectra were recorded in the region between 13957 and $14065\ \text{cm}^{-1}$, with a generation time of $300\ \mu\text{s}$ leading to an absorption equivalent pathlength of $45\ \text{km}$. For $^{13}\text{C}^{16}\text{O}_2$ the spectra were recorded at a pressure of 100 Torr using a photoacoustic spectrometer at Lille, in the regions around 13624 and $13726\ \text{cm}^{-1}$. Typically a time constant of 1 s and a sensitivity of $50\ \mu\text{V}$ were used for a laser power of 1.5 W.

The line were easily assigned owing to predictions obtained from a set of effective hamiltonian parameters determined through global fits to all available data collected from the literature. In the case of $^{12}\text{C}^{16}\text{O}_2$ the results of the global analysis have already been published ^a. For $^{13}\text{C}^{16}\text{O}_2$ the results of

^aS. A. Tashkun, V. I. Perevalov, J.-L. Teffo, L. S. Rothman and V. G. Tyuterev, *J. Quant.*

a global fit to more than 13000 experimental line positions will be presented. The RMS deviation from observed values reach 0.0015 cm^{-1} . Once included in the global fit, the line positions of the $2\nu_1 + 5\nu_3$ triad of $^{13}\text{C}^{16}\text{O}_2$ are reproduced with an accuracy similar to that obtained from the usual J polynomial expansion for separate bands, an within the accuracy of the measurements (0.01 cm^{-1}).

VIBRATIONAL POLYADS IN C₂H₂. INTER–POLYAD AND INTRA–POLYAD STRUCTURE

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Systematic analysis of quite different experimental data for the vibrational structure of acetylene molecule shows clearly the presence of global regular energy level patterns even at relatively high vibrational excitation^a. The purpose of the present poster is to demonstrate the relevance of simple models based on the polyad approach to describe the global structure of the system of vibrational states.

Natural classification of C₂H₂ vibrational states is based on the irreducible representations of the $D_{\infty h}$ group which is the symmetry group of the equilibrium configuration for this linear molecule. Essentially, this is a classification by the projection of the vibrational angular momentum k on the molecular axis. Further “good“ quantum numbers can be introduced taking into account the most important features of the intra-molecular dynamics. At low vibrational excitation each vibrational mode can be considered independently thus leading to a set of well defined number of quanta for each vibration like any sufficiently rigid molecule. In order to introduce quantum numbers which remain valid at high vibrational excitation we should look for approximately conserved quantities which are less dependent on separation of variables in harmonic approximation.

The approximate resonance relation between vibrational harmonic frequencies for C₂H₂ molecule $\nu_1 : \nu_2 : \nu_3 : \nu_4 : \nu_5 = 5 : 3 : 5 : 1 : 1$ enables one to introduce global polyad quantum number $N_r = 5n_1 + 3n_2 + 5n_3 + n_4 + n_5$ which plays the role of effective (properly counted) number of vibrational quanta. The most important anharmonic interactions introduced in a phenomenological way in order to reproduce the observed spectra preserve another sub-polyad quantum number $N_r = n_1 + n_2 + n_3$. One extra approximate quantum number $N_b = n_4 + n_5$ is useful to characterize purely bending excitations.

To describe pattern of vibrational energy levels within a simple model with a small number of parameters we start with global N_r -polyads giving for each polyad its energy and numbers of levels of each symmetry type. This

^aM. Herman, J. Liévin, J. Vander Auwera, and A. Campargue, *Adv. Chem. Phys* **108**, 1- 431 (1999)

is done through the generating function approach^b. Further splitting of N_r polyads into (N_r, N_s) polyads clearly shows the presence of regular structure which can be simply described as internal N_s structure of N_r polyads within the model with one internal degree of freedom. Again generating function approach enables us to calculate numbers of vibrational energy levels of certain symmetry within each sub-polyad.

Internal structure of $(N_r, N_s = 0)$ polyads is of special importance because it is relevant to any linear molecule with doubly degenerate modes in near 1 : 1 resonance. Global features of the quantum energy level system for $(N_r, N_s = 0)$ polyads are related to the topology and symmetry of the corresponding classical model.

^bD. A. Sadovskii and B. I. Zhilinskii. *J. Chem. Phys.* **103**, 10520-10536 (1995)

THE INTENSITIES OF METHANE IN THE 3 TO 5 μm REGION REVISITED

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The analysis of the line strengths of the infrared spectrum of methane (12 and 13) in the 3 to 5 μm region has been revisited on the basis of new measurements from Fourier Transform spectra recorded at Kitt Peak under various optical densities. A simultaneous fit of these new data with previously reported tunable double-frequency laser data has been done. An effective transition moment model in tensorial form up to the third order of approximation within the Pentad scheme has been used. The standard deviations achieved are very close to the experimental precision: 3 % and 1.5 % respectively for the two sets of data for the $^{12}\text{CH}_4$ molecule, representing a substantial improvement with respect to earlier studies. The integrated band strengths obtained in the present work differ from previously reported values by factors ranging from -5 % to +6 %. The correction for the ν_3 band, the strongest band of the Pentad system, is close to +2 % with respect to the study of Hilico et al. (*J. Mol. Spectrosc.* **168**, 455-476 (1994)). A list of ν_3 lines is proposed as secondary standards with absolute accuracies of 0.0002 cm^{-1} for positions and 2 % for intensities.

**ABSOLUTE LINE INTENSITIES IN THE $2\nu_2^0$ BAND OF
 $^{35}\text{ClCN}$ AND $^{37}\text{ClCN}$ AT 12.8 μm**

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Recently, the cyanogen chloride have been the subject of several studies at high resolution. Global analysis of vibration-rotation spectra have been realised by Fayt et al.^a, (see this paper for the references). In particular, the line positions (frequencies) of the $2\nu_2^0$ band have been measured using a diode laser spectrometer^b and a Fourier transform spectrometer^c. Very few results of intensities for ClCN can be found. In 1950, Nixon and Cross^d have determined, by integrated band method, the band strength of ν_1 and ν_3 . But, as we know, there is no study dedicated to the line intensities of the $2\nu_2^0$ band.

In the present work, we have recorded, with a tunable diode laser spectrometer, 63 absorption lines (35 of $^{35}\text{ClCN}$ and 28 of $^{37}\text{ClCN}$) to determine the absolute line intensities in the P- and R-branches of the $2\nu_2^0$ band. The lines with J value ranging from 3 to 53 have been located in the spectral range between 762 and 802 cm^{-1} , which have been covered by two Pb-Sn-Te diodes. Spectra have been recorded under a pressure ranging from 0.05 to 0.5 mbar, at room temperature and finally normalised to $T = 296$ K. For a given transition under study, four records have been made at different pressures, from which we have deduced an averaged value of the line intensity.

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CAVITY RING DOWN SPECTROSCOPY (CRDS) OF NO₂ IN
THE NEAR INFRARED REGION : ANALYSIS OF THE
 $\tilde{X}^2A_1-\tilde{A}^2B_2$ CONICAL INTERSECTION

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The high density and complexity of the visible NO₂ spectrum is mainly due to a conical intersection between the \tilde{X}^2A_1 and \tilde{A}^2B_2 Potential Energy Surfaces. This conical intersection induces strong vibronic interactions : a vibronic chaos is observed above 17000 cm⁻¹. At lower energy, i.e in the near IR, the $\tilde{X}^2A_1-\tilde{A}^2B_2$ interaction can be analysed in term of few interacting vibronic levels. The near IR absorption spectrum is very weak and locally perturbed. The high sensitivity of the CRDS technique combined with a supersonic slit expansion ($T_{rot}=15K$) allows us to record this spectrum at high resolution (about 200 MHz). We record the spectra of about 12 vibronic bands between 11000 and 12000 cm⁻¹. A rotational analysis gives the bands origins, the rotational and spin-rotation constants and reveal some rovibronic interactions. These band origins and intensity ratios are used to determined the mixing coefficients between the low lying \tilde{A}^2B_2 vibrationnal levels and the isoenergetics (resonant) high vibrationnal levels of \tilde{X}^2A_1 . The analysis of this $\tilde{X}^2A_1-\tilde{A}^2B_2$ interaction is done with the Domcke-Cederbaum conical intersection model.

**HIGH RESOLUTION CW CAVITY RING DOWN
SPECTROSCOPY (CRDS) FOR PROBING WEAK
MOLECULAR TRANSITIONS: UNEXPECTED NONLINEAR
TRANSITIONS IN JET-COOLED NO_2**

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For a ten of year, the CRDS technique emerges as a very powerful tool for probing weak absorption transitions of gaseous species or for probing traces of contaminants ($\alpha \sim 5.10^{-10}/\text{cm}$). Basically, this technique was associated with pulsed lasers (easy setup), however, by using CW lasers, it allows to reach a better resolution, Doppler-limited (here, molecules are seeded in a supersonic jet expansion), or even better if Doppler-free transitions can be observed.

The principle of the technique is simple, it consists in injecting a CW laser beam inside a Fabry Perot super cavity to increase the absorption path of the species under investigation (equivalent paths of a few km's are reachable). The measurement of the trapped energy decay time characterizes the intrinsic losses of the cavity itself, and the "losses" due to the sample under investigation (absorption). Exponential Ring Down decay times longer than $100 \mu\text{s}$ are obtained with the best mirrors available. This way, the absolute value of the absorption Beer-Lambert coefficient is determined.

However, CRDS spectra of NO_2 around 12500 cm^{-1} reveal nonlinear behavior, i.e., the decay time of numerous lines (in fact, hot bands) is non exponential, revealing a saturation effect (more than 20 W can be trapped inside the cavity) with can be exploited for the transition parameter determination.

Additionally to the CRDS measurement, the LIF signal can be simultaneously recorded. In our experimental setup, the PMT was blinded to the red energy range (i.e., the fluorescence emitted by the 1-photon absorbing levels could not be detected), however, every lines given rise to a CRDS signal, generates a similar LIF line pattern in the blue energy region, revealing 2-photon absorption transitions. Moreover, very thin transitions ($\sim 2 \text{ MHz}$) are also observable revealing coherent (resonant) 2-photon transitions.

This 2 kinds of transition will be discussed, but, if the existence of coherent 2-photon transitions for energy lower than the dissociation limit (25128.57 cm^{-1}) are easy to understand, the systematic existence of energy non selective incoherent 2-photon LIF transitions, even above the dissociation energy, is harder to understand, it looks like that a continuum of levels allows the 2-photon observed transitions without correlation with the known dissociation limit.

**SPECTROSCOPY OF XY_5Z (C_{4v}) SYMMETRIC TOP
MOLECULES : A TENSORIAL FORMALISM ADAPTED TO
THE $O(3) \supset O_h \supset C_{4v}$ CHAIN**

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High-resolution spectroscopy of XY_5Z molecules with C_{4v} symmetry is quite unknown both in infrared absorption and in Raman scattering. Moreover, these molecules are good candidates for photochemical reactions such as photodissociation. Thus, a better knowledge of the energy levels is needed.

Therefore, we propose a tensorial formalism adapted to the case of C_{4v} symmetric tops such as SF_5Cl , SF_5Br , SeF_5Cl , SeF_5Br , WF_5Cl , IOF_5 , ... It is an extension of the usual formalism already developed in Dijon for octahedral XY_6 molecules in the $O(3) \supset O_h$ group chain ^{a, b}.

We work in the $O(3) \supset O_h \supset C_{4v}$ chain because most of these symmetric tops result from the substitution of one ligand of the corresponding spherical tops and thus are close to octahedral symmetry. For example, SF_5Cl has a vibrational levels scheme similar to that of the SF_6 molecule.

Coupling coefficients and formulas for the computation of matrix elements of tensor operators are derived for this chain. Coupling coefficients are proposed for the C_{4v} group itself. We also give the expression of matrix elements of the Hamiltonian operator. Correspondance between the parameters of this model and usual ones is shown.

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TRANSITION MOMENTS FOR XY_5Z (C_{4v}) SYMMETRIC TOP MOLECULES USING THE TENSORIAL FORMALISM

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We present a development of the dipole and polarizability transition moments for XY_5Z symmetric top molecules with C_{4v} symmetry such as SF_5Cl , SF_5Br , SeF_5Cl , SeF_5Br , WF_5Cl , IOF_5 , ... These operators are involved in the calculation of rovibrational transitions intensities and are also needed for the evaluation of the Stark effect.

Therefore, we propose a development of the dipole moment and polarizability operators for XY_5Z (C_{4v}) symmetric top molecules, using a tensorial formalism derived from the one developed for octahedral molecules ^a. Formulas for the calculation of the matrix elements of the dipole moment and polarizability operators are given.

For practical applications we have built a program chain called C4VTDS devoted to the prediction of rovibrational spectra for both parallel and perpendicular bands, and more generally for any polyad scheme. These programs are presently limited to J values up to 96. This chain also includes spectrum calculation and hamiltonian parameter fitting programs and is analog to STDS (Spherical Top Data System ^b) or HTDS (Highly Spherical Top Data System ^c) softwares previously developed in Dijon for the T_d and O_h groups respectively.

As an example, this new tool should enable us to analyse the ν_1/ν_8 dyad of monoisotopic $SF_5(35)Cl$ which has been recorded thanks to a Bruker spectrometer in Wuppertal with an instrumental bandwidth of about 0.002 cm^{-1} (FWHM, unapodized). A very preliminary study will be presented.

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HIGH RESOLUTION FTIR AND PHOTOACOUSTIC OVERTONE SPECTRA OF HCCl

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High resolution vibration-rotation spectra of monochloroacetylene (HC-CCl) have been recorded in two different wavenumber regions. The FTIR measurements in the 4000 - 10000 cm^{-1} range have been recorded with a Bruker IFS 120 HR spectrometer in Wuppertal with a resolution of about 0.01 cm^{-1} . The photoacoustic measurements above 12000 cm^{-1} have been carried out with a titanium:sapphire ring laser (Coherent 899-21) spectrometer in Helsinki with the Doppler-limited resolution of about 0.02 cm^{-1} .

The aim of this study has been to provide as much accurate spectroscopic data (vibrational term values and rotational constants) as possible of the rovibrational states of monochloroacetylene and the resonances between the states. This kind of work builds the ground for the research of the dynamics of energy flow within a molecule, which is often referred as the intramolecular vibrational redistribution (IVR). Monochloroacetylene is a linear and relatively light molecule, producing rotationally resolvable overtone spectra. However, in the high wavenumber region, the structure of the spectra is already complicated enough due to the high density of the states, which makes the molecule appropriate for the energy flow studies.

INVESTIGATION OF H₂O OVERTONES BY LASER INDUCED FLUORESCENCE

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We have been measuring the laser-induced dispersed fluorescence spectra of water in the ground electronic state in the near infrared range. The same method has previously been used to study the highly excited vibrational overtones of acetylene (HCCH) raising up questions, which require further investigation. If the local mode state [40-] of acetylene is pumped, a molecular collision between an excited molecule and an unexcited molecule may change the local mode state from [40-] to [40+]. The energy difference between these two local mode states is about 4 cm⁻¹.

In this study, we have been investigating if the same kind of collision-induced transitions between the paired local mode states could appear while the energy difference is larger. As an appropriate test molecule, we have used water pumping different single vibration-rotation lines of the local mode state [21-]. The energy difference between [21-] and [20+] states is about 164 cm⁻¹.

Another interesting feature is related to the possible lower states in the vibrational transition. According to a simple local mode theory, if the [21-] state is pumped, two emission bands with equal intensities should appear. This corresponds to two different cases: 1) the quantum number of the first OH-bond oscillator is decreasing by one giving [11+] as the lower state 2) the quantum number of the second OH-bond oscillator is decreasing by one giving [20+] as the lower state.

The cell containing the sample at the room temperature has been placed inside a Ti:Sapphire ring laser cavity. The fluorescence signal has been collected by a parabolic mirror and directed into a high resolution FTIR-spectrometer. The dispersed fluorescence has been detected in the 2800 - 4000 cm⁻¹ range. Many collision-induced rovibrational transitions from the [21-] state have been observed per one pumping line.

CAVITY RING DOWN SPECTROSCOPY ON CARBON CHAIN RADICALS

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A sensitive and generally applicable technique for direct absorption spectroscopy on electronic transitions of carbon chain radicals in the gas phase is presented. These species are thought to be important as possible *diffuse interstellar band* carriers, but electronic gas phase spectra are still rare. The method is based on cavity ring down spectroscopy in a pulsed slit nozzle, incorporating a discharge in a high pressure supersonic expansion. The performance is demonstrated on spectra of the origin bands of the typical ${}^2\Pi \leftarrow X^2\Pi$ electronic transitions of linear carbon chain radicals $C_{2n}H$ ($n=3-6$), $HC_{2n}H^+$ ($n=2-4$), $HC_{2n+1}N^+$ ($n=2$) and $NC_{2n}N^+$ ($n=1-3$). For most of the chains rotationally resolved and rotationally cold spectra ($T_{rot} < 15$ K) have been obtained. The sensitivity of the technique is demonstrated for anions with a detection limit as low as 10^7 C_2^- -molecules cm^{-3} for rovibrational transitions of the $B^2\Sigma_u^+ \leftarrow X^2\Sigma_g^+$ system. The band origins are compared to the list of diffuse interstellar bands.

**TUNABLE FAR INFRARED SPECTROSCOPY OF $^X\text{KRH}^+$
AND $^X\text{KRD}^+$ ($X=82,84,86$)**

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Pure rotational absorption spectra of the krypton hydride ion in its ground electronic and vibrational state have been measured in the 0.5 - 3.5 THz range for six different isotopic configurations with tunable far infrared spectrometers. The ions are generated in LN₂ cooled hollow cathode and magnetically extended negative glow discharges. The accurate frequency measurements determine the rotational constants B, D and H and yield transition frequencies accurate to 40 kHz (1 σ). By combining all results a mass independent Dunham analysis has been performed, yielding accurate information on the Born Oppenheimer breakdown parameters.

MICROWAVE SPECTROSCOPY OF 1-CHLORO-1,1-DIFLUOROETHANE

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We report^a further investigation of the millimeter-wave rotational spectrum of the 1-Chloro-1,1-difluoroethane ($\text{CH}_3\text{CF}_2\text{Cl}$, HCFC-142b)^b. In the frequency range between 50 and 120 GHz we have measured about 600 line frequencies for the ground state of $\text{CH}_3\text{CF}_2^{35}\text{Cl}$, about 500 for the ground state of $\text{CH}_3\text{CF}_2^{37}\text{Cl}$, and about 300 for the first torsional state of $\text{CH}_3\text{CF}_2^{37}\text{Cl}$. In the treatment of the observed rotational spectra we have used approach adapted for the analysis of unresolved hyperfine structure of transitions^c. High accuracy of new measurements and extended range of quantum number J up to 99 gave an opportunity to improve significantly sets of rotational parameters for the ^{35}Cl and ^{37}Cl isotopomers in the ground state. For the first torsional state of ^{37}Cl isotopomer the complete set of rotational parameters as well as centrifugal distortion and quadrupole coupling parameters were obtained for the first time. For some transitions of this state small A-E internal rotation splittings were observed.

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MILLIMETER-WAVE SPECTRUM OF CF_2Cl_2

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The rotational spectrum of the ground state of $CF_2^{35}Cl_2$ molecule was investigated in the frequency range from 60 to 100 GHz. New measurements gave an opportunity to improve rotational and quartic distortion parameters by order of magnitude and to determine 6 sextic centrifugal distortion parameters. In the analysis of the spectrum we have used our high-precision (accuracy 5kHz) and fast-scan (accuracy 50kHz) measurements^a as well as data available in literature. Special technique was used to process line profiles of unresolved or partially resolved hyperfine structures of rotational transitions. It allowed us to improve significantly diagonal parameters of quadrupole coupling χ_{aa} , ($\chi_{bb}-\chi_{cc}$) and to determine off-diagonal parameter χ_{ab} . The profiles of 18 unresolved transitions and frequencies of isolated lines were fitted simultaneously. The results and used approach are discussed in details^b.

^aThe most recent description of used spectrometer is available in the paper: V. V. Ilyushyn, E. A. Alekseev, S. F. Dyubko, O. I. Baskakov, *J. Mol. Spectrosc.* **195**, 246-255 (1999)

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WIDE-RANGE MILLIMETER-WAVE SPECTROMETER

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The communication^a presents up-to-date state of automated millimeter-wave spectrometer at Kharkov Laboratory. Since the time of the most recent description of the spectrometer^b it has undergone a number of significant improvements.

The computer-controlled millimeter-wave frequency synthesizer is used as a radiation source of the spectrometer. The continuous lock-in frequency range of the spectrometer is 50 - 145 GHz. This gives an opportunity to realize two main synthesizer-based operating modes of the spectrometer: fast-scan and high-precision. Fast-scan mode is intended for initial studies of molecular rotational spectra when it is necessary to record very wide frequency ranges. Frequency determination error is determined by a frequency step of corresponding record and is about 30 kHz. High-precision mode is used on the final stages of spectrum investigations when the highest accuracy and resolution are required. Frequency determination error for isolated line in this mode doesn't exceed 5 kHz when signal-to-noise ratio is better than 10.

Spectral resolution is limited by Doppler broadening of observed spectral lines. Sub-Doppler resolution is achieved by means of Lamb dip observation. Estimated sensitivity is about 10^{-8}cm^{-1} .

^aThis work was supported by INTAS under INTAS-UKRAINE project 95-UA-0187.

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**INFLUENCE OF THE COLLISION PARTNER (He AND Ar)
ON LINE-MIXING EFFECTS IN THE ν_3 INFRARED BAND
OF METHANE AT ROOM TEMPERATURE**

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Line-mixing effects are studied in the ν_3 band of CH₄ perturbed by Ar and He at room temperature. Experiments have been made in the 2800 – 3200 cm⁻¹ spectral region using four different set ups. They cover a wide range of total densities, including low (0.25 – 2 atm), medium (25 – 100 atm), and high (200 – 1000 atm) pressure conditions. Analysis of the spectra demonstrates that the spectral shapes (of the band, the Q branch, the P and R manifolds, ...) are significantly influenced by line mixing. In the theoretical approach proposed in order to model and analyze these effects, semiclassical state-to-state rates are used together with a few empirical constants^b. Comparisons between measurements and spectra computed with and without the inclusion of line mixing are made. They prove the quality of the approach which satisfactory accounts for the effects of pressure and of rotational quantum numbers on the spectral shape. It is shown that collisions with He and Ar lead to different line-coupling schemes (e.g. more coupling within the branches and less between branches) and hence to different shapes. The influence of line coupling between different branches and manifolds is evidenced and studied using high pressure spectra and absorption in the band wings.

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THE MILLIMETER- AND SUBMILLIMETER-WAVE
SPECTRUM AND THE DIPOLE MOMENT OF
ETHYLENIMINE, $c\text{-C}_2\text{H}_4\text{NH}$

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The rotational spectrum of ethylenimine (aziridine, aza-cyclopropane) has been investigated in selected frequency regions from 118 GHz to 950 GHz using the Cologne Terahertz Spectrometer. About 320 lines have been measured spanning the quantum numbers $2 \leq J \leq 59$ and $0 \leq K_c \leq 50$. Moreover, FTMW-measurements have been performed at the ETH Zürich to redetermine the dipole moment and to improve hyperfine constants (3 transitions, 20 lines, 9–24 GHz). All lines have been fitted in consideration of previously published data to yield refined ground state constants such as $A = 22736.19294$ (31) MHz, $B = 21192.46114$ (31) MHz, and $C = 13383.16401$ (30) MHz and centrifugal distortion constants that permit accurate predictions of transition frequencies for the astronomical community.

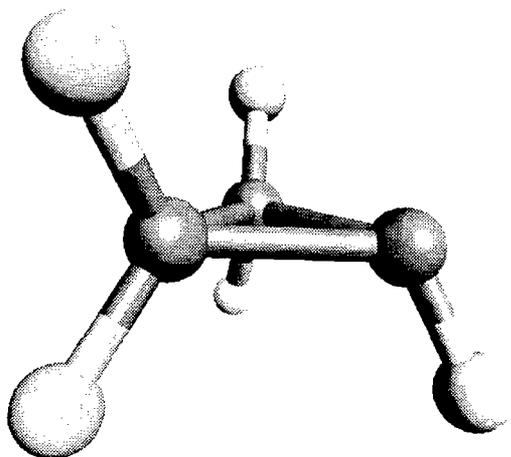


Figure 1: Molecular structure of ethylenimine

SUB-DOPPLER MEASUREMENTS ON THE ROTATIONAL TRANSITIONS OF HYDROGEN CYANIDE

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The hyperfine structure of HCN could be resolved by saturation dip measurements using the Cologne terahertz spectrometer. The interaction between the electric field gradient of the electrons and the electric quadrupole moment of the nitrogen nucleus causes the splitting of energy levels with different quantum number F . This small splitting in rotational transitions can only be measured by means of sub-Doppler spectroscopy. The measured spectra of HCN exhibits not only Lamb dips but also crossover dips, from which the frequency differences of blended hyperfine components were determined. These saturation dip measurements of HCN in its vibrational ground state and in the first and second excited vibrational state for $J = 5 \leftarrow 4$, $J = 6 \leftarrow 5$, $J = 7 \leftarrow 6$, and $J = 8 \leftarrow 7$ (from 443 to 708 GHz) result in an improved accuracy for the hyperfine constants $eQq_{(^{14}N)}$ and $C_{(^{14}N)}$. Concerning astrophysics it is interesting to compare the ratios of the intensities of the hyperfine components measured in the laboratory to astrophysically obtained HCN spectra, since this allows the optical depths of astrophysical objects to be determined.

**A HIGH RESOLUTION INFRARED STUDY OF THE
NASCENT NO PRODUCED IN THE REACTION
 $\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$**

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Both NO and OH are molecules of atmospheric interest, and their role in atmospheric chemistry has been subject of many studies. Although the kinetics of the reaction $\text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH}$ has been studied in detail in scattering experiments, little is known about the internal energy distribution of OH and NO. We used infrared spectroscopy to characterize the internal energy distribution of the nascent NO. From scattering and LIF experiments it appears that most of the excess energy in this exothermic reaction is taken up by the OH radical and that the NO molecule is relatively cold. Our flow tube consist of three parts in borosilicate, interconnected with teflon fittings. A flow of 3 % H_2 in Ar mixture passes through a MW discharge where about 25-50 % of the H_2 is dissociated. The H atoms which are formed react with a mixture of 2% of NO_2 in Ar, at the exit of a second tube which ends in a perforated bulb. A tunable diode laser is used to detect the reaction products in a small White cell. From infrared absorption intensities and linewidths we deduced that the NO produced is practically formed at ambient temperature with a small fraction (about 2 %) of the molecules in the $v=1$ state. Various reaction parameters were varied to study their influence on the produced NO concentration. Recently we tested new diode laser sources around $2.9 \mu\text{m}$ to investigate the OH radical through infrared absorption measurements.

SUB-DOPPLER DIODE LASER JET SPECTROSCOPY OF FREONS

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It is well known that many trace compounds present in the stratosphere play an important role in atmospheric chemistry and are held responsible for phenomena like the greenhouse effect, acid rains and the partial destruction of the protective ozone layer. Therefore a constant monitoring and mapping of the concentration of these compounds in the stratosphere is desirable. Interpretation of solar transmission spectra requires accurate molecular constants as well as line broadening parameters which in many cases are not available for important trace gases. The analysis of high resolution infrared spectra can provide the required accurate molecular parameters.

The difficulty in analysing infrared absorption spectra of freons is due to the extremely high line density in the spectra, caused by the presence of a dense rotational structure, and the superposition of spectral structure of different isotopic species and hot bands. The complexity of these spectra can be reduced by supersonic jet cooling. Typically rotational temperatures of about 20 K can be obtained by seeding the compound of interest in a noble gas carrier, and vibrational cooling, though not as efficient as the rotational cooling, reduces the hot band intensities. Some examples of high resolution diode laser jet spectroscopy can be found in [1,2]. The ν_1 band of CCl_3F could be analysed for the three major isotopic species by rotational cooling up to 20 K[2].

Recently we have obtained high resolution diode laser spectra of some freons using a new molecular jet apparatus in combination with multipass optics. In our set-up the laser beam crosses the molecular jet perpendicularly about 20 times at a distance of a few mm from the pulsed source. Spectra were recorded by synchronising the gas pulse to a fast laser scan (500 μs) and averaging the absorption spectra on a fast oscilloscope. Small portions of the laser beam were directed respectively through a confocal etalon and an absorption cell containing CHClF_2 at low pressure. High resolution calibrated FTIR spectra of this molecule were made available by Prof. Martin Quack and provided a secondary frequency standard which was used to calibrate the jet spectra.. We consider this calibration procedure more accurate than that of using few lines of a primary frequency standard, due to the non-linear behaviour of laser frequency with respect to the laser current. Diode laser jet spectra will be presented for some of the most important freons.

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TEMPERATURE DEPENDENCES OF
PRESSURE-BROADENING, PRESSURE-SHIFTING AND LINE
MIXING DUE TO AIR IN THE ν_3 BAND REGION OF $^{12}\text{CH}_4$

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The temperature dependence of the off-diagonal relaxation matrix elements has not been previously determined for CH_4 . In the present work we have attempted to determine the temperature dependences of air-broadening, pressure-shifting and line mixing for $^{12}\text{CH}_4$ transitions in the ν_3 band region by analyzing high-resolution infrared spectra of methane recorded with two Fourier transform spectrometers (FTS). More than 50 laboratory absorption spectra of $^{12}\text{CH}_4$, $^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$ obtained at various temperatures (-60 °C to +25 °C) with the McMath-Pierce FTS (0.01 cm^{-1} resolution) and with the FTS at the LPMA at Orsay (0.003 cm^{-1} resolution) were fit simultaneously using the multispectrum nonlinear least-squares fitting technique^a. Absorption cells with pathlengths from 1.7 cm to 2500 cm and pressures from less than a torr to more than 500 torr were used in obtaining the spectra. Spectra recorded with 98% pure CH_3D , 99% pure $^{13}\text{CH}_4$, natural samples of CH_4 , and lean mixtures ($\approx 1\%$) of both $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in dry air have been fit simultaneously in order to obtain consistent results.

The line mixing model incorporated into the least-squares fitting procedure determines separate relaxation matrix coefficients related to air-broadening and self-broadening. It is possible to determine the temperature dependence exponents for the broadening, shifting and the off-diagonal relaxation matrix coefficients associated with line mixing. Comparisons of present results with previous results in the literature will be discussed.

diode laser spectra of supersonic jets and isotopically enriched samples", *J. Chem. Phys.* 103(20), 8846-8853 (1995)

^aD. Chris Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and D. Atkins, *JQSRT* **53**, 705-721 (1995).

PROGRESS IN HIGH-INFORMATION TIME-RESOLVED FOURIER TRANSFORM SPECTROSCOPY

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At first glance, the three decades old Fourier transform spectroscopy may be considered as inappropriate for solving problems involved in modern dynamic studies. With the most up-to-date interferometers, recording an interferogram is a lengthy process when considering the typical requirements of time resolution. Only recently have the specific virtues of FTS applied to short time duration phenomena become more evident^a.

The present paper reports the instrumental progress made with the step-scan interferometer of LPPM, for time-resolved applications, particularly as used for the high resolution infrared domain. The interferometer is now improved^b so to routinely record time-resolved interferograms. 10^3 high resolution spectra each made of 10^6 samples may be recorded in 5 hours with a time resolution up to 2 ns and a spectral resolution up to $2.5 \cdot 10^{-3} \text{ cm}^{-1}$. Experimental solutions to overcome the difficulties related to the dynamic range, the time-resolution and the important amount of data are described.

Sequences of time-resolved Doppler-limited spectra of argon/hydrogen and nitrogen/helium mixtures have been recorded around $5 \mu\text{m}$. They describe the temporal behaviour of 10 kHz ac electrical discharges with a time resolution of the order of $1 \mu\text{s}$.

^asee for instance:

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C.D. Pibel, E. Sirota, J. Brenner, and H.-L. Dai, "Nanosecond time-resolved FTIR emission spectroscopy: monitoring the energy distribution of highly vibrationally excited molecules during collisional deactivation", *Journal of Chemical Physics* **108**, 1297-1300, 1998.

G. Durry, G. Guelachvili, "N₂(B-A) Time-Resolved Fourier Transform Emission Spectra from a Pulsed Microwave Discharge", *Journal of Molecular Spectroscopy* **168**, 82-91, 1994.

R.A. Palmer, J.L. Chao, R.M. Dittmar, V.G. Gregoriou, and S.E. Plunkett, "Investigation of time-dependent phenomena by use of step-scan FT-IR", *Applied Spectroscopy* **47**, 1297-1310, 1993.

^bN. Picqué, "Espèces Moléculaires. Approches Nouvelles par Spectroscopie de Fourier." Thèse de Doctorat en Sciences, Spécialité Lasers et Matière, n. d'ordre 5593, Université de Paris-Sud, (1998).

**PRECISE LINE STRENGTHS AND BROADENING
PARAMETERS FOR THE $2\nu_1 + 2\nu_2^0 + \nu_3$ COMBINATION
BAND OF CO₂ AROUND 1575 nm BY DIODE LASER
SPECTROSCOPY**

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The $2\nu_1 + 2\nu_2^0 + \nu_3$ combination band of CO₂ has been studied with an extended cavity diode laser spectrometer in the wavelength range 1567-1580 nm, and line strengths and collision broadening parameters for self broadening and nitrogen broadening have been determined with a standard uncertainty of 2%. The results show significant deviations from existing data bases, in particular for high-J values of the R branch.

WATER VAPOR LINE PARAMETERS IN THE 3500-3650 cm^{-1} REGION

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Pressure broadening and pressure-induced shift coefficients due to water and nitrogen have been determined for water vapor transitions in the 3500-3650 cm^{-1} region. The temperature dependences of the widths and shifts have also been determined for selected transitions in this region. Results have been compared with values available in the literature. The line parameters have been obtained from the analysis of room temperature recordings of the spectrum of pure water and recordings of the spectra of heated water/nitrogen and water/air mixtures. The recordings of the water vapor spectrum were obtained with Fourier Transform Spectrometers at Kitt Peak and at the Justus-Liebig-Universität Giessen. Up to eleven spectra have been fitted simultaneously with a multispectrum nonlinear least-squares fitting technique^a.

^aD. Chris Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and D. Atkins, *JQSRT* **53**, 705-721 (1995).

ON THE NEW HIGH RESOLUTION STUDY OF THE
ROTATIONAL STRUCTURES OF THE AsH_3 VIBRATIONAL
STATES (0200), (0101), AND (0002)

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Fine rotational structures of the (0200), (0101), (0002, A_1), and (0002, E) vibrational states were reanalyzed. For this purpose, high resolution Fourier transform spectrum of the AsH_3 was recorded in the region of the first deformational overtones and of the $\nu_2 + \nu_4$ combination band. As the further analysis shown, additional information about hot bands $2\nu_2 - \nu_2$, $2\nu_4 - \nu_4$, $\nu_2 + \nu_4 - \nu_4$, and $\nu_2 + \nu_4 - \nu_2$ is very useful, especially in determination of the upper energies with the low values of quantum number J . On this reason, additional spectrum was recorded near the 2 μm region.

Numerous resonance interactions both between the different vibrational states, and inside of E -type vibrational states were detected, and corresponding Hamiltonian model was used for analysis.

The $a_1 - a_2$ splittings in the spectrum were found and described not only for the low values of the quantum number $K = 1, 2, 3$, or 4, but for high values $K = 5, 6, 7, 8$, and even 11.

Parameters of the Hamiltonian, which were determined by the least square fit procedure, reproduce the initial experimental data with good accuracy.

THE GROUND AND FIRST TORSIONAL STATES OF DEUTERATED ACETALDEHYDE: LINE POSITION AND HYPERFINE STRUCTURE ANALYSES

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The pure rotational spectra of the ground and first excited torsional states ($v_t = 0$ and 1) in the 8–254 GHz frequency range and the high resolution far infrared pure torsional spectrum ($v_t = 1 \leftarrow 0$ band) have been recorded for 2,2,2- d_3 -acetaldehyde (CD_3CHO). A data set consisting of 1016 $v_t = 1 \leftarrow 0$ far infrared torsional lines together with 195 microwave lines within $v_t = 0$ and 79 microwave lines within $v_t = 1$ has been considered in a near-to-experimental-accuracy analysis carried out using a global RAM approach, which was successfully used in the past for the normal species of acetaldehyde. The final fit includes lines with J up to 20 and requires 25 parameters to achieve root-mean-square deviations of 87 and 88 kHz for the microwave lines within $v_t = 0$ and 1, respectively, and of 0.00048 cm^{-1} for the far infrared lines.

An analysis of the hyperfine structure of some of the pure rotational microwave lines has also been undertaken. The Fourier transform microwave spectrometer coupled with a pulsed molecular beam, in the university of Valladolid, was used to record the hyperfine patterns. The high resolution achieved by this spectrometer was necessary to resolve the quadrupole coupling hyperfine splittings arising from the three deuterium atoms.

In addition to the line position analysis, the results of the hyperfine structure analysis will be presented. This second analysis should provide us with values for the quadrupole coupling constants of the three nonequivalent deuterium atoms and should allow us to determine the effects of the large amplitude internal rotation on the hyperfine energy level pattern. Deuterated acetaldehyde displays a tunneling splitting of 209 MHz, *i.e.*, much larger than the deuterium hyperfine coupling. For this reason, an averaging of the quadrupole coupling of the three deuterium atoms is expected. This is confirmed by the measurements carried out for the A and E -type components of the $1_{01} \leftarrow 0_{00}$

transitions for which the hyperfine patterns could be fully resolved and analyzed. Measurements have been carried out for other tunneling rotational transitions. They display a more complicated hyperfine pattern which has not yet been analyzed.

GENERALIZED SIMULATED ANNEALING METHOD IN THE ANALYSIS OF ATOM-ATOM INTERACTION

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The techniques of generalized simulated annealing are presented in this work in a way to fit the external turning points of a diatomic potential energy curve. In order to evaluate the advantages of this method, the long-range part of the potential energy curve for the $A^1\Sigma_u^+$ electronic state of the ${}^6\text{Li}_2$ molecule is treated using the multipolar expansion and the asymptotic exchange energy considering the gradual change from a Hund's case a to c . The results are carefully compared with previous determinations using conventional fitting methods of molecular spectroscopy.

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IODINE ATLAS AS FREQUENCY REFERENCE ONLINE

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The low uncertainty of highly precise frequency measurements of few optical transitions of a molecular spectrum can be transferred to larger ranges through the knowledge of the relevant molecular parameters. The prospects of this concept were investigated for the spectrum of the I₂ molecule. In the range from 778 nm to 816 nm the frequencies of altogether 37 rovibronic transitions were measured¹ with a relative uncertainty of $\frac{\delta\nu}{\nu} = 1 \dots 3 \cdot 10^{-10}$. With some additional measurements of frequency differences a set of Dunham parameters could be derived, which allows an interpolation of transition frequencies with an uncertainty of < 100 kHz ($\frac{\delta\nu}{\nu} = 3 \cdot 10^{-10}$) in this spectral range. Based on these precise values and together with precise transition frequencies taken from literature mainly for the red and green part of the spectrum, highly precise potentials for the X and the B state could be derived. A computer program will be demonstrated, which allows calculation of the iodine spectrum in the range from 820 nm to 530 nm including hyperfine structure with a prediction uncertainty of ≤ 10 MHz. The Doppler-free hyperfine structure can be displayed in a magnified scale. Additionally, the well known iodine atlas by Gerstenkorn and Luc was recalibrated, so that it can be used now with an uncertainty of 30 MHz. The limits of this concept will be discussed.

¹ Measurements partly in cooperation with Physikalisch Technische Bundesanstalt (PTB) Braunschweig

THE APPARENT DISORDER OF THE Rb_2
 $A^1\Sigma_u^+(0_u^+) \sim b^3\Pi_u(0_u^+)$ SPECTRUM RESOLVED: A CASE OF
FULLY COUPLED ELECTRONIC STATES

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The [$A^1\Sigma_u^+(0_u^+) \sim b^3\Pi_u(0_u^+)$] pair of excited electronic states in Rb_2 , coupled through spin-orbit interaction, has been studied through the fluorescence spectra of the $(2)^1\Pi_g \rightarrow [A \sim b]$ transition, recorded by FTS. These states in alkali dimers are a well-known example of perturbations between molecular states [1]. Instead of the expected observation of monotonic series of lines depicting vibrational series and rotational multiplets of a given electronic states, unusual spectra show up, characterized by oscillating spectroscopic constants over a large range of transition energies (several hundreds of cm^{-1}). Similar behavior is also predicted in Cs_2 .

In order to analyze these data, we have computed the eigenvalues of the [$A \sim b$] pair of states, using the recently developed Fourier grid Hamiltonian method [2]. We show that in contrast with lighter alkali dimers, vibrational levels from both potentials are mixed over almost all the binding energy range. The resulting spectroscopic constants are found in excellent agreement with experimental data, allowing in several cases the assignments of unknown lines in the spectra [3]. Comparison of these results with recent photoassociation data from D. Heinzen's group should enforce the validity of our model.

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IR SPECTRA OF THE OPEN SHELL IONIC
COMPLEXES $\text{H}_2\text{O}^+-\text{Rg}_n$

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Infrared photodissociation spectra of the open shell ionic complexes $\text{H}_2\text{O}^+-\text{Rg}$ ($\text{Rg} = \text{He}, \text{Ne}, \text{Ar}$) and $\text{H}_2\text{O}^+-\text{Ar}_n$ ($n=1-9$) ionic complexes have been recorded in the vicinity of the OH stretch vibrations. The spectra of the proton-bound dimers are rotationally resolved and provide thus detailed information about structure and bonding in these simple open shell complexes. The analysis of frequency shifts and photofragmentation branching ratios in the spectra of larger clusters give insight into the microsolvation process (structures and binding energies). The interpretation of the spectra is guided by ab initio calculations.

EFFECTS OF ELECTRON-SPIN ON THE INFRARED SPECTRUM OF THE O₂-HF COMPLEX

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We have developed a theoretical model^a for calculating rotational energy levels and line intensities of rotational transitions in oxygen complexes. The model predicts the pattern of the observed^b rotational transitions in the O₂-HF/O₂-DF complex. For each J, there are nine states correlating to $\Sigma = 0, \pm 1$ spin components of the ground electronic state of O₂ and the K = 0, ± 1 manifold of the complex. Three of these transitions belong to the K = 0 manifold, whereas six transitions belong to the K = ± 1 manifold. Relative intensities of transitions correlating to K = 0 are stronger than those correlating to K = ± 1 .

We have applied the model for assignment and fitting of the observed infrared spectrum of the O₂-HF/O₂-DF complex. We have obtained a good fit for the prominent triplet structure in the observed infrared spectrum of the O₂-DF complex. This fit includes about seventy transitions correlating to the $\Sigma = 0, \pm 1$ spin components of the ground electronic state of O₂ corresponding to K = 0, P = 0, ± 1 manifolds of the complex and J = 0 to J = 11. The standard deviation of that fit is about 0.0002 cm⁻¹, which is in good agreement with the experimental precision. A comparable fit was obtained for the O₂-HF complex. The standard deviation of that fit is about 0.0009 cm⁻¹, which is about four times larger than the standard deviation of the O₂-DF fit. The molecular parameters obtained from the least squares fits indicate that the O₂-DF complex is more rigid than the O₂-HF complex and that both complexes have a nonlinear geometry.

Assignment and analysis of transitions correlating to the $\Sigma = 0, \pm 1$ spin components of the ground electronic state of O₂ and to K = ± 1 , P = 0, $\pm 1, \pm 2$ manifolds of the complex are currently in progress. Results of analysis and least squares fits of the observed infrared spectrum of the O₂-HF/O₂-DF complex will be presented.

^aWafaa M. Fawzy, *J. Mol. Spectrosc* 160, 84-96 (1993); Wafaa M. Fawzy, *J. Mol. Spectrosc.* 191,68-80 (1998).

^bThese data were taken by Chris Lovejoy in David Nesbitt's laboratory at JILA.

THE HIGH RESOLUTION INFRARED SPECTRUM OF THE WEAKLY-BOUND VAN DER WAALS COMPLEX Ne-CH₄ IN THE 7 μm REGION ($j=1 \leftarrow 0$ TRANSITIONS)

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The infrared spectrum of the weakly bound rare gas-spherical top complex Ne-CH₄ in the region of the triply degenerated vibration ν_4 of CH₄ has been recorded. Measurements were made by a tunable diode laser spectrometer using a pulsed nozzle for the production of complexes in a supersonic jet. Three branches were observed (respectively resolved *P*- and *R*-branches and an unresolved *Q*-branch) correlated with the *R*(0) transition of the methane monomer at 1311.4 cm⁻¹. The absorption pattern in the spectrum of Ne-CH₄ is much denser and more close to the *R*(0) line of CH₄ than in the previously measured spectra of Ar-CH₄ and Kr-CH₄. However, by analogy with the spectra of Ar-CH₄ and Kr-CH₄, assignment and analysis could be done using a Hamiltonian model incorporating Coriolis interaction between the angular momentum of CH₄ and the end over end rotation of the complex. The spectra of Ne-CH₄, Ar-CH₄, and Kr-CH₄ and the results of our analysis will be presented.

Further, the spectroscopical study of these complexes in the region of CH₄ *Q*(1) and *R*(1) is in progress as already done for the $j=0 \leftarrow 1$ transitions corresponding to CH₄ *P*(1) at 1300.3 cm⁻¹.

**OBSERVATION OF THE ν_3 FUNDAMENTAL
BAND OF HBr^+**

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The ν_3 (B-Br stretch) fundamental bands of $\text{H}^{11}\text{B}^{79}\text{Br}^+$ and $\text{H}^{11}\text{B}^{81}\text{Br}^+$ molecular ions have been detected for the first time in the spectral range of 900 to 970 cm^{-1} , using a tunable infrared diode laser spectrometer along with the velocity modulation detection technique. The ions were produced in the positive column of an ac glow discharge containing a mixture of H_2 and BBr_3 . Thirty-three lines have been assigned for each isotopomer up to $J'' = 40$. The molecular parameters have been obtained using a polynomial expansion series up to the second order. They reproduce the data within the experimental uncertainty (0.003 cm^{-1}). *Ab initio* calculations of the band origins and the internuclear distances have been performed using the Gaussian 94 package. The calculated values are in highly satisfactory agreement with the experimental results.

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EXCITATION SPECTROSCOPY OF THE FeF RADICAL

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The (0,0) bands of the systems at 330 nm (${}^6\Phi - {}^6\Delta$) and 325 nm (${}^6\Pi - {}^6\Delta$)^a of FeF have been recorded at Doppler-limited linewidths by Laser Induced Fluorescence. The results have been analysed and used to determine much better parameters for FeF in the excited state, using the known parameters from the millimeter-wave spectra for the ground state, ${}^6\Delta$ ^b. FeF was produced by the reaction of fluorine atoms, produced by a microwave discharge of fluorine in helium, with iron pentacarbonyl.

^aB. Pouilly, J. Schamps, D. J. W. Lumley and R. F. Barrow, *J. Phys B: Atom. Molec. Phys.*, **11**, 2289, (1978).

^bM. D. Allen and L. M. Ziurys, *J. Chem. Phys.*, **106**(9), 3494, (1997)

ON THE EQUILIBRIUM STRUCTURE AND DIPOLE MOMENT OF CIS-1-CHLORO-2-FLUOROETHYLENE

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In order to determine the electric dipole moment of cis-1-chloro-2-fluoroethylene, the Stark spectrum of several rotational transitions in the 12–24 GHz frequency region was observed at dry ice temperature for different electric fields. Measurements were carried out in a Stark cell built with a P band wave-guide and using a computer controlled frequency synthesizer as centimeter-wave source. A zero based 10 kHz square-wave-modulated electric field was applied to the cell electrodes, with the lock-in amplifier tuned to that frequency, so that the zero field spectrum is 180° out of phase with respect to the Stark components.

The experimental spectrum profile was fit to a model function computed as a sum of Lorentzian profiles over the hyperfine-Stark components. In order to derive the frequencies of such components, a Fortran code was written to compute the energy levels for a given electric field by diagonalizing the full Rotational-Quadrupole-Stark Hamiltonian matrix.

The equilibrium geometry and the dipole moment of cis-1-chloro-2-fluoroethylene were evaluated using different *ab initio* methods: CCSD(T) and MP4. In these calculations we employed the correlation consistent triple-zeta (cc-pVTZ) basis set of Dunning .

Since the Hartree-Fock (HF) determinant dominates the electronic molecular wavefunction, accurate predictions were given by coupled cluster theory with single and double excitations including a perturbative treatment of the triple substitutions, which usually determine the most important higher contributions. Since full inclusion is rather expensive, we used CCSD(T) method, which is a good approximation to take into account triple excitations. Fourth order Møller-Plesset many-body perturbation theory (MP4), including single, triple and quadruple substitutions from the HF configuration, were also employed and gave very close estimates of the equilibrium geometry and the molecular dipole moment.

Being CCSD(T) and MP4 post-Hartree-Fock methods, the dipole moment was estimated numerically as energy derivative with respect to an applied electric field at zero field strength.

All calculations were carried out using the MOLPRO suite of programs^a.
Experimental and computational details will be presented.

^aMOLPRO is a package of *ab initio* programs written by H. -J. Werner and P. J. Knowles, with contributions of J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Ebert, C. Hampel, W. Meyer, K. Peterson, R. M. Pitzer, A. J. Stone, P. R. Taylor.

MODE SELECTIVE STEREOMUTATION AND INVERSION IN ANILINE: HIGH RESOLUTION INFRARED SPECTROSCOPY AND 36-DIMENSIONAL HAMILTONIAN APPROACH

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The inversion motion in aniline and the related stereomutation of the chiral isotopomer C_6H_5-NHD has been of interest for some time as a prototype system for stereomutation and enantiomerisation in general [1,2].

We investigate the influence of all vibrational modes on the NH_2 inversion tunneling dynamics of aniline [3,4]. The infrared absorption spectrum of aniline was recorded between 10 and 10000 cm^{-1} . The spectrum is analysed in terms of a reaction path Hamiltonian using an ab initio potential energy surface. The large amplitude motion is chosen as reaction path and is treated explicitly on a grid. All other internal degrees of freedom are treated adiabatically in the harmonic approximation. The theoretical treatment includes as essential extension of previous reaction path treatments [5] the method of diabatic rotations, which decouples degenerate modes occurring at certain values of the reaction coordinate. This approach has also been successfully applied to the torsion motion of hydrogen peroxide and tested by comparison to full 6D calculations [6] on an analytical global potential hypersurface [7]. We discuss the application to the inversion process in aniline, the theoretical relation to the reaction path hamiltonian treatment in [3], as well as to the concepts arising from the adiabatic channel model [8].

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THE VIBRATIONAL-ROTATIONAL ENERGY LEVELS OF SILANONE

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The equilibrium structure and six-dimensional potential energy surface of silanone, H_2SiO , has been determined from large-scale *ab initio* calculations using the coupled-cluster method, CCSD(T), with basis sets of double- through quintuple-zeta quality. The effects of core-electron correlation on the calculated structural parameters have been investigated. The anharmonic force field has been determined. The vibrational-rotational energy levels of the molecule have then been calculated using variational and perturbational methods. The calculated molecular properties are found to be in good agreement with experimental data.

MOLECULAR SPECTROSCOPY OF PHASE TRANSITIONS IN LIQUID CRYSTALS

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University, Prospect Glushkova 6, 252022 Kyiv, Ukraine

The vibrational Raman spectroscopy allows to obtain information about the molecular structure changes under a structural transformations in various substances. Earlier we find that there is correlation between molecular conformations and structure of the supercooled mesogeneous substances in their different phases^{a, b}. The aim of our work was to investigate the molecular thermoconformations in the supercooled mesogeneous objects such as MBBA and ABT (p-aminoxybenzylidene-p-toluidine).

We realized the shock cooling of our samples and it's slow heating. Then it was investigated the temperature dependencies of vibrational bands frequencies in heating cycle after shock cooling. The frequencies of the vibrational bands shift under phase transitions. The widths of the bands at first decrease with increasing of the temperature (T=203 K - MBBA, T=213 K - ABT). These temperature points was interpreted as amorphous phase - metastable crystal transition. Shift and broadening of around 2 cm^{-1} of some vibration Raman bands at following heating (T=263 K - MBBA, T=293 K - ABT) correspond to metastable crystal - stable crystal phase transition and corresponding conformational changes of the molecules^c. After transformations of crystal phase in mesogeneous state the widths and frequencies of bands are similar with same parameters in amorphous state. It allows us to conclude that at shock cooling nematic structure was frozen^{d, e}.

Besides the structural and conformational relaxation processes of ABT at temperature points before amorphous state - metastable crystal transition (T=198, 210 K) was investigated. It was obtained the time dependencies of vibrational band widths and estimated relaxation times at these temperatures: $\tau_{198K} \sim 120\text{ min}$, $\tau_{210K} \sim 250\text{ min}$. Note that the final values of bandwidths coincide with widths for metastable crystal phase.

^aV.Ye. Pogorelov, *Solid State Physics* **33**, 1906 (1991).

^bV.Ye. Pogorelov, I.B. Estrela-Llopis, *Mol. Cryst. Liq. Cryst.* **265**, 237 (1995).

^cV.Ye. Pogorelov, I.P. Pinkevich, I.B. Estrela-Llopis, V.P. Bukalo, *Mol. Cryst. Liq. Cryst.* **320**, 29 (1998)

^dV.Ye. Pogorelov, I.P. Pinkevich, I.B. Estrela-Llopis, V.P. Bukalo, *Proceedings SPIE* **3488**, 68 (1998).

^eV.Ye. Pogorelov, I.B. Estrela-Llopis, I.P. Pinkevich, W.P. Bukalo, *Mol. Cryst. Liq. Cryst.* **301**, 377 (1997).

Also the transformation of amorphous phase of ABT into metastable crystal is developed in decreasing of vibration band 1174 cm^{-1} and appearance and increasing of band with frequency 1177 cm^{-1} . It's connected with existence of different molecular conformations in these phases. But after annealing of sample at $T=198, 210\text{ K}$ we did not observe the disappearance of conformer with characterizing for amorphous state the band 1174 cm^{-1} . The final ratio of intensities of bands 1177 and 1174 cm^{-1} is around $1/2$ in two temperature points. The time of conformational relaxation is around 50 min . So due to comparison of relaxation times it was found that the processes of structural relaxation and conformational changes at amorphous state - metastable crystal transformation are not correlated.

Invited Lectures E

Tuesday, September 7, 9:00

Chairman : L. ROTHMAN

SPECTROSCOPY OF NEARLY-DISSOCIATING MOLECULES^a

ALAN CARRINGTON, *Department of Chemistry, University of Southampton, Hampshire SO17 1BJ, UK*

We have developed a technique for studying the spectra of molecular ions involving energy levels lying within a few wavenumbers of the dissociation asymptote. This is in contrast to most spectroscopic studies which are concerned with molecules at or near their ground state equilibrium configurations. We use an ion beam method in which the ions are formed by electron impact ionisation of a flowing gas or neutral molecular beam. Passage of the beam through an electric field lens leads to fragmentation of the very weakly bound levels, and the fragment ions produced are energy-analysed and detected. Spectroscopic transitions induced prior to the electric field lens result in population transfer, producing detectable changes in the fragment ion current. We have used microwave radiation, from 6 GHz to 170 GHz. Our initial work was concerned with the hydrogen molecular ion and its deuterium isotopes. We will review this work very briefly, and then describe recent work on two species. The first is the neon dimer ion, for which we have been able to characterise the details of the potentials for four electronic states correlating with the lowest dissociation limit. Our experimental results lead to a complete map of the rovibronic levels lying within ten wavenumbers of the dissociation asymptote. The second molecular species to be described is the complex formed between the hydrogen molecular ion and a helium atom. Microwave transitions reveal the presence of both ortho and para species, clearly distinguishable by the presence or absence of proton hyperfine structure. Provisional assignments of two transitions will be presented, and related to current ab-initio potential functions.

^aThis talk is a Molecular Physics Lecture supported by Taylor & Francis Ltd

HIGH RYDBERG STATES AND HIGH RESOLUTION SPECTROSCOPY

F. MERKT, *Laboratorium für Physikalische Chemie, ETH Zürich, CH-8092 Zürich, Switzerland*

Over the past ten years pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy (PES) has evolved into a powerful and reliable spectroscopic technique [1-3]. The technique relies on the pulsed field ionization of very long-lived high Rydberg states ($n \geq 100$) located immediately below successive molecular ionization thresholds. Stark mixing by stray electric fields in the experimental volume is responsible for the long lifetimes [4,5].

The talk will first review the recent progress that has enabled the improvement of the resolution of PFI-ZEKE-PES to its current limit of 0.2 cm^{-1} [6,7]. At this resolution, which is almost comparable to the bandwidth of commercial pulsed dye lasers, the technique can not only be used to obtain detailed spectroscopic information on molecular ions, but also to study unstable, short-lived neutral molecules [8].

Strategies will then be outlined that may lead to further improvements in the resolution of PFI-ZEKE-PES. The strategy followed in Zurich relies on very high resolution (60 kHz) spectroscopic measurements on high Rydberg states using a vacuum ultraviolet-millimeter waves double-resonance technique [9]. This technique enables, on the one hand, precise spectroscopic measurements of the energy level structure of high Rydberg states just below the ionization thresholds. On the other hand, it permits the determination and compensation of the stray electric fields in the experimental volume to an accuracy of $\pm 20 \mu\text{V/cm}$ [10]. Under conditions where stray fields and ion concentrations are minimized, only the highest molecular Rydberg states ($n \gg 500$) are sufficiently long lived to be detected, and the resolution of PFI-ZEKE-PES is improved. This strategy will be illustrated by high-resolution spectroscopic measurements on the CH_4^+ ion, an ion on which hardly any high-resolution spectroscopic data had been reported until recently [11].

This work is supported financially by ETH Zürich and the Robert Gnehm Stiftung.

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Poster Session F
Tuesday, September 7, 11:00

**HIGH RESOLUTION PFI-ZEKE PHOTOELECTRON
SPECTROSCOPY OF THE FIRST ELECTRONIC
STATES OF Kr_2^+**

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CH-8092 Zürich, Switzerland*

The first electronic states of Kr_2^+ have been investigated by high resolution pulsed field ionization zero kinetic energy (PFI-ZEKE) photoelectron spectroscopy.

The spectra, which were recorded in the range between 103500 cm^{-1} and 118200 cm^{-1} (12.83-14.65 eV) using a broadly tunable XUV laser source, reveal extensive vibrational progressions associated with the ground $A\ 2\Sigma_{1/2}^+$ ionic state of the most abundant isotopomers of Kr_2 .

From the spectra accurate adiabatic ionization potentials and potential energy functions are extracted for the ground and several electronically excited states of Kr_2^+ .

This work is supported financially by ETH Zürich and the Robert Gnehm Stiftung.

m_j -PREFERENTIAL PREDISSOCIATION IN THE $D^1\Sigma_u^+$ STATE OF THE Cs_2 MOLECULE

M. BABA, *Faculty of Integrated Human Studies, Kyoto University, Kyoto 606-8501, Japan*; **Y. KIMURA, S. KASAHARA, and H. KATO**, *Faculty of Science, Kobe University, Kobe 657-8501, Japan*

Cs_2 is strongly predissociative in the higher vibrational levels of the $D^1\Sigma_u^+$ state and the dissociation is enhanced by the external magnetic field. We have observed the Zeeman spectrum of the Cs ($8s^2S_{1/2} \leftarrow 6p^2P_{3/2}$) transition and determined the relative population for each m_j level of the dissociated $\text{Cs}(^2P_{3/2})$ atom. The observed predissociation rate was strongly dependent on m_j . It is of great interest that the $m_j = +1/2$, and $+3/2$ levels are preferentially populated than $m_j = -1/2$, and $-3/2$, respectively.

The $D^1\Sigma_u^+$ state does not directly couple with the $(2)^3\Sigma_u^+$ state which is the dissociative state correlating to $\text{Cs}(6p^2P_{3/2}) + \text{Cs}(6s^2S_{1/2})$. Therefore, it is the indirect predissociation in which the $D^1\Sigma_u^+$ state is coupled with the $(2)^3\Sigma_u^+$ state by spin-orbit interaction and this state is coupled with the $(2)^3\Sigma_u^+$ state by L -uncoupling and Zeeman interactions.

By the theoretical consideration of predissociation rate, it is concluded that the m_j dependence arises from different strength of the interaction for three $^3\Sigma_u^+$ levels whose energies are split in the magnetic field.

We also observed the Doppler profile of the spectral line and the recoil direction of dissociated atoms have been shown to be selective for each m_j level.

VUV PHOTODISSOCIATION PATHWAYS OF C₂H₂ VIA
RYDBERG STATES STUDIED WITH
SYNCHROTRON RADIATION

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C. FELLOWS^a, N. SHAFIZADEH and D. GAUYACQ ,
*Laboratoire de Photophysique Moléculaire, Bât. 210,
Université Paris-Sud, Orsay, France*

The photodissociation of the acetylene molecule is studied in this work using synchrotron radiation between 180 to 60 nm in free gas flow. Some new results concerning the photodissociation processes will be related presenting new light about the pathways and the concerned products of the reactions.

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RESONANT 2-PHOTON IONIZATION STUDY of AlND_3 COMPLEX: EXCITED ELECTRONIC STATES

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AlND_3 complexes are produced in a Smalley-type laser ablation source and probed by resonant 2-photon ionization technique. Six progressions of bands are observed in the range 18100-26200 cm^{-1} . Four progressions are assigned to the $\tilde{\text{B}}^2\text{A}_1\text{-}\tilde{\text{X}}^2\text{E}$, $\tilde{\text{C}}^2\text{E-}\tilde{\text{X}}^2\text{E}$, and $\tilde{\text{E}}^2\text{A}_1\text{-}\tilde{\text{X}}^2\text{E}$ electronic transitions, with the $\tilde{\text{B}}^2\text{A}_1$ state correlating to the $\text{Al}(4s\ ^2\text{S})+\text{ND}_3(^1\text{A}'_1)$ limit, the $\tilde{\text{C}}^2\text{E}$ and $\tilde{\text{E}}^2\text{A}_1$ states to the $\text{Al}(3d\ ^2\text{D})+\text{ND}_3(^1\text{A}'_1)$ limit, and the $\tilde{\text{X}}^2\text{E}$ state to the $\text{Al}(3p\ ^2\text{P})+\text{ND}_3(^1\text{A}'_1)$ limit. The origin bands of the $\tilde{\text{B}}^2\text{A}_1\text{-}\tilde{\text{X}}^2\text{E}$, $\tilde{\text{C}}^2\text{E-}\tilde{\text{X}}^2\text{E}$, and $\tilde{\text{E}}^2\text{A}_1\text{-}\tilde{\text{X}}^2\text{E}$ transitions are located at $18532.5\pm 0.7\ \text{cm}^{-1}$, $21185\pm 5\ \text{cm}^{-1}$, and $22667\pm 2\ \text{cm}^{-1}$, respectively. The spin-orbit splitting of the ground state is determined to be $55.8\pm 0.7\ \text{cm}^{-1}$. Wavenumbers of the following vibrations are measured: ν_3 (Al- ND_3 stretch) in the $\tilde{\text{B}}^2\text{A}_1$ state equal to $316.0\pm 0.8\ \text{cm}^{-1}$, ν_3 and ν_6 (Al- ND_3 bend) in the $\tilde{\text{C}}^2\text{E}$ state equal to $428\pm 2\ \text{cm}^{-1}$ and $594\pm 12\ \text{cm}^{-1}$, respectively, and ν_3 in the $\tilde{\text{E}}^2\text{A}_1$ state equal to $358\pm 2\ \text{cm}^{-1}$. Assignments of two progressions remain uncertain. Partially resolved rotational structure of some of the bands is observed and analyzed. Rotational constants of the various P-levels of the ground state are measured to be $B\approx 0.23\text{-}0.24\ \text{cm}^{-1}$, in good agreement with calculated value of $0.227\ \text{cm}^{-1}$. The adiabatic ionization potential of the AlND_3 complex is measured by photoionization efficiency technique as equal $39710\pm 10\ \text{cm}^{-1}$. Rydberg series converging to various levels of the $\text{Al}^+\text{-ND}_3$ stretching mode of the AlND_3^+ cation are observed. The ν_3^+ frequency is determined to be $322\ \text{cm}^{-1}$. The AlND_3 complex has approximate C_{3v} symmetry. The structure determination of the neutral and monopositive complex and assignment of vibrational modes are aided by *ab initio* calculation.

PHOTOASSOCIATION SPECTROSCOPY OF THE PURE LONG-RANGE STATES IN Cs₂

CLAUDE AMIOT, DANIEL COMPARAT, ANNE CRUBELLIER, CYRIL DRAG, OLIVIER DULIEU, ANDREA FIORETTI, BRUNO LABURTHE, FRANCOISE MASNOU-SEEUWS, PIERRE PILLET, *Laboratoire Aimé Cotton, CNRS II, Bât.505, Université Paris-Sud, 91405 Orsay Cedex, FRANCE*

Ultrahigh precision spectroscopy of alkali dimers can now be achieved using two complementary techniques: the well-established Fourier transform spectroscopy (FTS) at room temperature, and the more recent photoassociative spectroscopy in cold atom traps. Moreover, accurate theoretical spectroscopic predictions are also available, due to continuous efforts for computation of molecular potential curves over wide range of internuclear distances and excitation energies.

In this contribution, we present two examples of results obtained in our laboratory, involving the collaboration between the three approaches above, concerning the two pure long-range states [1] of the Cesium dimer, which are responsible of the first observation of translationally cold molecule formation [2]:

1) We have analyzed the external well of the $0_g^-(6s + 6^2P_{3/2})$ pure long-range state in Cs₂ (correlated to the $(1)^3\Pi_g$ state at short distances), detected by photoassociation spectroscopy [3]. Due to its location at intermediate internuclear distance (about $20a_0$), the full characterization of this well required the use of molecular spectroscopy fitting methods (RKR and NDE), and quantum chemistry calculations [4,5]. The 0_g^- state is predicted to have a double-well structure, where the wells are separated by a potential barrier at an energy close to $6s + 6p_{3/2}$. Further FTS studies should provide a correct description of this barrier.

2) The external well of the $1_u(6s + 6^2P_{3/2})$ pure long-range state in Cs₂ (correlated to the $b^1\Pi_u$ state at short distances), has also been analyzed using the same technique [6]. This state is accurately described using standard asymptotic methods based on multipolar expansion of the atom-atom interaction energy, including also molecular hyperfine structure. A very good agreement with experiment has been obtained, both for energy positions and line intensities.

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ULTRA-HIGH RESOLUTION SPECTROSCOPY IN THE INFRARED REGION USING A SUPERSONIC BEAM OF SF₆

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During the last twenty years high resolution spectroscopy in the 10 μm spectral region has reached a resolution at the level of the kHz ^a. To improve this performance, the main point is to reduce the transit broadening. We recently used the slow molecules detection method and obtained some linewidths (HWHM) of the order of a few 100 Hz ^b, but with a degraded signal.

Alternatively to this cell spectroscopy we are now exploring the possibility of a molecular beam for high resolution spectroscopy and metrology. A well-known technique to reduce the transit broadening is to apply the method of separated fields. In the optical domain it must be associated with a Doppler-free technique. We have thus developed a Doppler-free two-photon Ramsey fringes experiment with a supersonic beam of SF₆. With two interaction zones separated by 8 cm, we recorded some fringes with a periodicity of 2.3 kHz ^c. With more than 10 fringes, the central frequency was determined with a precision of 10 Hz. This Ramsey method seems very promising, since the present setup has the potential to increase the interzone distance as well as the resolution by an order of magnitude. This system is thus a very serious candidate for a frequency standard in the infrared region with a potential accuracy in the 10⁻¹⁴ – 10⁻¹⁵ range.

This work was supported by the Bureau National de Métrologie, the ETCA-DRET, the European Union through two HCM programs and the Gonville and Caius College.

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^cL.F. Constantin *et al.*, submitted to Phys. Rev. A

**STRIKING ANHARMONIC RESONANCES IN N₂O₄:
SUPERSONIC JET FOURIER TRANSFORM SPECTRA AT
13.3, 7.9, 5.7 AND 3.2 μm**

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The spectrum of N₂O₄ has been obtained at ULB in the 3.2, 5.7, 7.9 and 13.3 μm regions, using a supersonic slit jet system coupled to a Fourier transform spectrometer with a spectral resolution of 0.005 cm^{-1} . Analysis of the spectra obtained indicates that the temperature of the molecular beam is close to 30 K. In the 3 lowest frequency spectral regions, not only were the ν_9 , ν_{11} , and ν_{12} fundamental bands observed, but each fundamental was accompanied by a strong combination band which appears because of a strong anharmonic resonance leading to a transfer of intensity from the fundamental band to the combination band. All the bands were successfully analyzed leading to ground state combination differences which were combined with those obtained in a previous diode-laser study,^a and fitted to obtain ground state rotational constants. The upper state energy levels were fitted using an Hamiltonian which explicitly takes into account the anharmonic resonances. The experimental data could be fitted to within their experimental uncertainties.

^aJ.L. Domenech, A.M. Andrews, S.P. Belov, G.T. Fraser, and W.J. Lafferty, *J. Chem. Phys.*, **100**, 6993-6999 (1990).

FTIR SPECTROSCOPY IN A SUPERSONIC LAVAL NOZZLE

ROBERT GEORGES, ABDESSAMAD BENIDAR, ROGER LE DOUCEN, and JOËL BOISSOLES, *Équipe de Spectroscopie Infrarouge - Laboratoire PALMS UMR 6627 CNRS-Université de Rennes I, Campus de Beaulieu, 35042 Rennes, France*

We have developed a new experimental set-up devoted to the spectroscopic investigation of stable and weakly bound molecules in the infrared domain at very low temperatures using the CRESU (Cinétique de Réaction en Écoulement Supersonique Uniforme) facilities which avoid the problem of condensation experienced in cryogenic cooling. This approach was developed at the université de Rennes by Rowe and co-workers for the study of molecular processes at very low temperatures^a. The CRESU apparatus offers an ultra-cold and homogeneous gas-phase medium produced by a controlled supersonic expansion. Such a supersonic flow is prepared by an adiabatic expansion through a convergent-divergent nozzle so-called a Laval nozzle. The great Mach number uniformity of the produced isentropic flow allows to work under precise and *a priori* known temperature, pressure and density conditions. Temperatures range from 10 to 170 K according to the used Laval nozzle, while the gas density n is relatively high (10^{16} - 10^{17} molecules.cm⁻³) when compared to a free jet expansion. Moreover, the isentropic region extends over a length ℓ of few tens of centimetres which yields to a product $n \times \ell$ of 10^{18} - 10^{19} molecules.cm⁻² which is very interesting for an absorption based experiment. Our high resolution Fourier transform interferometer BRUKER IFS120HR has been then interfaced to such a uniform supersonic jet system. Our experimental set-up was successfully tested with the recording at 26 K of the spectrum of the ν_5 band of the NO strongly bound dimer (Dissociation energy of 8.5 kJ.mol⁻¹) which will be presented^b. We orient now our efforts towards the observation at very low temperature of small hydrocarbures as methane (CH₄) and very weakly bound molecules (Dissociation energy about 1 kJ.mol⁻¹).

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^bA. Benidar, R. Georges, J. Boissoles, S. Hamon, A. Canosa and B.R. Rowe, *in preparation*.

HIGH RESOLUTION INFRARED SPECTROSCOPIC STUDY OF THE ν_3 BAND OF ReF_6 IN A SUPERSONIC JET EXPANSION

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Transition-metal hexafluorides constitute a very interesting class of molecules since some of these species are stable open-shell systems. A good example is rhenium hexafluoride, ReF_6 , which exhibits a fourfold degenerate electronic ground state of G'_g symmetry (in the O_h^S group^a). This situation leads to very complex rovibronic couplings^{b,c} that constitute a break-down of the Born-Oppenheimer approximation. McDowell and Asprey^d noticed many years ago a very unusual low resolution band profile for the $\nu_3(F_{1u})$ stretching fundamental.

However, no high resolution study has been realized up to now. This is due *i*) to the very high reactivity of this species and *ii*) to the high number of hot bands in the room temperature spectrum of such a heavy molecule, making it impossible to study at high resolution without efficient cooling. We have developed in the past in the Zürich laboratory a unique facility, which allows for a combined study of high resolution supersonic jet spectra by means of FTIR spectroscopy (BOMEM DA002, instrumental band width unapodized 0.0024 cm^{-1}) and diode laser spectroscopy^{e,f}. For the present study the system was improved with respect to resistance to chemically aggressive compounds.

We have recorded survey FTIR spectra of the ν_3 fundamental band of ReF_6 in a continuous supersonic jet expansion. Due to the weakness of the absorption, the instrumental bandwidth was limited to 1 cm^{-1} (FWHM, unapodized). Different $\text{ReF}_6:\text{He}$ and $\text{ReF}_6:\text{Ar}$ mixtures were used. The spectra show a rather weak and very broad band with a complex profile, far from the usual *PQR* pattern.

Some parts of this band have also been recorded with 0.0007 cm^{-1} bandwidth using the diode laser pulsed slit jet facility^f. A multiple-pass set-up has

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^c V. Boudon, M. Rotger and D. Avignat, *J. Mol. Spectrosc.*, **175**, 327–339, (1996).

^d R.S. McDowell and L.B. Asprey, *J. Mol. Spectrosc.*, **45**, 491–493, (1973).

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^f H. Hollenstein, M. Quack and E. Richard, *Chem. Phys. Lett.*, **222**, 176–184, (1994).

been used to observe low-intensity lines. In this case, we have used a ReF_6 :He mixing with a seeding ratio 1:4 leading to a rotational temperature estimated to 50 K. The rovibronic lines were resolved for the first time, showing a very dense and complicated structure.

In both experiments, special care was taken to handle this extremely reactive species in the jet.

A very preliminary interpretation of the results is presented. These seems to support the expectation of a quadratic vibronic coupling leading to four ($G'_g \otimes F_{1u} = E'_{1u} \oplus E'_{2u} \oplus 2G'_u$) strongly interacting vibronic sublevels.

SPONTANEOUS RAMAN SPECTROSCOPY OF CLOSED AND OPEN-SHELL TRANSITION-METAL FLUORIDES

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Hexafluorides molecules form a large family of both closed and open-shell systems. In the present work they have been synthesized in Jerusalem and their spontaneous Raman spectroscopy has been re-investigated in Lille thanks to a sensitive CCD detection, which enables us to work at room temperature ^a (i.e. at the corresponding vapor pressure, a few hundred Torr). This spectroscopy has already been studied a long time ago by Claassen and Selig ^b, but with a lower sensitivity and resolution, and over a temperature range (from 25° to 150°) which did not allow them to observe faint vibronic structures due to pressure broadening.

The $\nu_2(E_g)$ and $\nu_5(F_{2g})$ bands are Raman active. They have been observed in detail for different transition-metal groups. For open-shell systems (ReF_6 , OsF_6), complicated band profiles have been recorded. This is mainly due to the complex rovibronic effects (such as the Jahn-Teller effect, ...) existing in these species which possess a degenerate electronic ground state. As a result the usual *OP-Q-RS* structure is not observed.

We give some comparisons between these spectra and the results obtained from higher electronic transitions (which enabled indirect determination of ground state Jahn-Teller parameters) ^{c,d,e}. A simple model for the vibronic polarizability is presented and Raman vibronic selection rules are deduced. As a first result these rules allow the interpretation of the observed band profiles ^{d,e}.

We also present the Raman bands of the IF_7 heptafluoride. This spectrum should be helpful in the determination of the molecular structure of this molecule, which is still an open question ^{f,g}.

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^bH.H. Claassen and H. Selig, *Israel Journal of Chemistry*, **7**, 499-504, (1969).

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**ROTATIONAL SPECTRA OF THE $3\nu_{18}$, $\nu_{11}+\nu_{18}$, AND ν_{17}
VIBRATIONAL STATES OF CF_3CFH_2**

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The rotational spectra of the $3\nu_{18}$, $\nu_{11}+\nu_{18}$, and ν_{17} excited vibrational states of CF_3CFH_2 molecule were measured in the frequency range from 50 to 140 GHz with accuracy not worse than 10kHz. The rotational and centrifugal distortion parameters for these excited vibrational states were obtained for the first time. The assignment of observed rotational spectra to corresponding vibration states is based on intensity considerations and previous investigation of the ground, ν_{18} , $2\nu_{18}$, and ν_{11} excited vibrational states^a. We have revealed small perturbations of the rotational spectra of $3\nu_{18}$ and $\nu_{11}+\nu_{18}$ states. This corresponds to our prediction made on the basis of observed interaction between the $2\nu_{18}$ and ν_{11} vibrational states. The assignment of measured lines and analysis of interaction between $3\nu_{18}$ and $\nu_{11}+\nu_{18}$ states are discussed^b.

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^bThis work was supported by INTAS under INTAS-UKRAINE project 95-UA-0187.

THE WATER VAPOR CONTINUUM IN THE MMW REGION. THE ROLE OF VARIOUS MIXING GASES

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The continuum of water vapor, observed in the gaps between the line centers called atmospheric windows, does not follow laws describing the behavior of conventional lineshapes based on the impact approximation, like the Van Vleck-Weisskopf profile. After laboratory experiments at 239 GHz in atmospheric conditions implying H₂O-H₂O and H₂O-N₂ collisions, the aim of the present investigations is now the nature of the continuum, which is not completely understood. Absolute absorption measurements of water vapor with various X mixing gases are thus carried out at the same frequency^{a,b}.

The last data concern X = CH₄, C₂H₄ and C₂H₆, where the characteristics of continuum are present, i.e. a higher magnitude of absorption, a stronger temperature dependence and a non negligible H₂O pressure term. For the H₂O-CH₄ mixture, semi-classical calculations of halfwidths and their temperature dependence are presented. The influence of quadrupole, when it exists, is shown ; collision induced absorption (CIA) of the X gases may be involved in the absorption process, although the X pressure squared term of absorption gets cancelled in the experimental procedure.

^aA. Bauer, M. Godon, J. Carlier and R.R. Gamache, *J. Mol. Spectrosc.* **176**, 45-57 (1996)

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**THE EFFECT OF PULSED MAGNETIC, RF AND ELECTRIC
FIELDS ON MOLECULAR COHERENCES STUDIED WITH
QUANTUM BEAT SPECTROSCOPY**

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Recently we demonstrated the application of a pulsed magnetic field for creating and manipulating coherences in molecules and employing quantum beat spectroscopy to monitor the time evolution of the superposition states, using CS₂ as an example.^a Here we present the application of precisely tailored magnetic pulses to the creation and phase control of molecular coherences^b and to the manipulation of coherences and populations among Zeeman levels in a static magnetic field. In addition we compare and contrast these results with those obtained previously in our group using pulsed radio frequency (RF) fields.^c Finally we present preliminary results on the analogous Stark experiment where a pulsed electric field is used to create coherences between asymmetry doublets in the asymmetric top molecule propynal HCCCHO.

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^cH. Bitto, A. Levinger and J. R. Huber, *Z. Phys. D* **28**, 303 (1993)

THE STRETCHING FUNDAMENTALS OF SbD_3

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The ν_1 (A₁) and ν_3 (E) stretching fundamental bands of both ^{121}Sb and ^{123}Sb isotopomers of deuterated stibine, SbD_3 , have been recorded at high resolution (0.0027 cm^{-1}) between 1250 and 1470 cm^{-1} using a BRUKER 120 HR interferometer. A total of about 2500 rotation-vibration transitions have been assigned with J' and K' up to 22. Several $\Delta k = \pm 3$ "perturbation allowed" transitions have been identified, mainly in the ν_3 band. The ν_1 (symmetric Sb-D) and ν_3 (antisymmetric Sb-D) stretchings are nearly degenerate, the band origins being at 1358.5 and 1362.4 cm^{-1} , and at 1358.3 and 1362.2 cm^{-1} , for $^{121}SbD_3$ and $^{123}SbD_3$, respectively. 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. In addition, the ground state combination differences obtained from the assigned transitions, together with the pure rotational transitions measured in the far-infrared region, provided accurate values for the ground state spectroscopic parameters, including the k-dependent ones, C and D_K , and the $\Delta k = \pm 3$ interaction constants, ϵ , ϵ_J , and ϵ_K .

**ANALYSIS OF HIGH RESOLUTION SPECTRA OF $^{18}\text{O}_3$ IN
THE REGION 1600-1900 cm^{-1}**

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We have recorded high resolution infrared spectra of $^{18}\text{O}_3$, using the Fourier Transform Spectrometer of Reims, and a large pathlength x product (3216 cm x 6.0 Torr).

In the 1600-1900 cm^{-1} region, we have observed and analysed the dyad ($\nu_1 + \nu_2$, $\nu_2 + \nu_3$), considering line positions and intensities, as well as the corresponding hot bands $\nu_1 + 2\nu_2 - \nu_2$, $2\nu_2 + \nu_3 - \nu_2$.

We give here Hamiltonian parameters, for both dyads, as well as transition moment parameters, the range of observed transitions and the statistics of the fits.

**COMPLETE ANALYSIS OF THE TETRAD
(003)/(102)/(201)/(300) INTERACTING STATES
OF $^{16}\text{O}_3$ MOLECULE**

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The 2850 – 3360 cm^{-1} spectral range is revisited for an accurate determination of highly excited rotational levels of (003), (102), (201) and (300) vibrational states of ozone. For calculations of these states we took into account the Darling-Dennison resonances between (300) and (102) states and (003) and (201) states as well Coriolis resonances between (003) and (102), (102) and (201), (201) and (300) states. The fit on 2315 energy levels determined from observed transitions with $J_{\max} \leq 65$ and $K_{a\max} \leq 20$ gives a r.m.s. $< 9.5 \times 10^{-4} \text{ cm}^{-1}$ and provides a satisfactory agreement between calculated and observed energy levels.

The interactions of this tetrad with other polyads were also analyzed. The perturbation of energy levels of the (201) state ($K_a < 2$, $27 < J < 35$) by the (130) state are described by a Coriolis resonance. In addition, an interaction of the tetrad with the (210) state of the triad (012)/(111)/(210) has been found. The energy levels of the (003) state ($J \geq 20$, and $K_a < 16$) and the (102) state ($K_a < 12$, $35 < J < 50$) are perturbed by levels of the (210) state with $K_a < 17$ and $K_a < 14$ respectively.

Line intensities have been measured and fitted, leading to the determination of transition moment parameters for the fourth bands. Using these parameters we have obtained the estimations for the integrated band intensities. The general line listing of the $3\nu_3$, $\nu_1+2\nu_3$, $2\nu_1+\nu_3$, and $3\nu_1$ bands (up to $J_{\max} < 70$ and $K_{a\max} < 25$) has been generated with an intensity cutoff $10^{-26} \text{ cm}^{-1}/\text{mol cm}^{-2}$.

These calculations are of interest for the spectroscopic data banks. The complete line listing in the 2850 – 3360 cm^{-1} region is available on request from the authors.

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THE HIGH-RESOLUTION INFRARED SPECTRUM OF THE SYMMETRY FORBIDDEN BAND, ν_5 , OF $^{10}\text{B}_2\text{H}_6$

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Because of its interesting hydrogen-bridged structure, diborane B_2H_6 has been the subject of numerous spectroscopic studies over the years. Although diborane is an asymmetric top molecule, it has relatively high symmetry, belonging to the D_{2h} point group, which includes a center of symmetry, and the rule of mutual exclusion applies where Raman and IR bands do not coincide. There is only one totally inactive vibration, ν_5 , (A_u), the BH_2 torsional mode. However, in the early 1950's Lord and Nielsen^a assigned a very weak infrared band at 829 cm^{-1} to ν_5 . They attributed its optical activity to a Coriolis resonance with the energy levels of the very strong fundamental, ν_{18} .

We have recorded the spectrum of ^{10}B monoisotopic diborane from 700 to 1800 cm^{-1} at high resolution ($2 - 3 \times 10^{-3}\text{ cm}^{-1}$) using the Bruker 120 HR interferometer at Wuppertal equipped with a long path cell in order to observe the ν_5 region as well as other stronger bands. The ν_5 band has been observed at 832.845 cm^{-1} and consists of a well resolved Q-branch accompanied by weaker P- and R-branch lines. Since this band is forbidden, its intensity is "borrowed" from the ν_{18} band at 1178 cm^{-1} via an A-type Coriolis resonance. Very anomalous line intensities are seen with the low K_a transitions being vanishingly weak. The selection rules are $\Delta K_a = \text{even}$; $\Delta K_c = \text{even}$. About 120 transitions with J and K_a ranging from 4 to 23 and 4 to 19 respectively have been assigned. An analysis of this band is in progress. The results of this analysis as well as those of other bands will be reported.

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ROTATIONAL ANALYSIS OF THE ν_7 BAND IN FURAN (C₄H₄O)

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We have investigated the infrared absorption spectrum of the ν_7 fundamental band in furan (C₄H₄O) at 995 cm⁻¹. Fourier transform spectroscopy was used at Bruxelles to record the spectrum under room temperature conditions at 0.01 cm⁻¹ instrumental resolution. Diode laser spectroscopy in a 40 Kelvin supersonic jet was used at Lille to resolve the fine rotational structure around the band center.

Finally some 5,559 FT lines and 101 DL transitions were assigned in this work and are fitted separately and simultaneously, in different procedures, each time constraining the ground state constants to their literature value.^a The molecular constants resulting from this fit using a Watsonian with a S reduction, in I^r and III^r representation, are provided and discussed.

^aG. Wlodarczak, L. Martinache, J. Demaison, and B.P. Van Eijck, *J. Mol. Spectrosc.* **127**, 200-208 (1988).

HIGH RESOLUTION INFRARED SPECTROSCOPY OF SMALL CARBON CLUSTERS

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Pure carbon chain molecules have no permanent dipole moment and thus no pure rotational spectra. Their extremely low bending vibrations are therefore of great interest for astrophysical detection in cold interstellar clouds. Small carbon clusters C_n ($n \leq 13$) have been produced in a laser ablation supersonic jet source in amounts that are sufficient for direct laser absorption spectroscopy in the mid infrared region. We present high resolution tunable diode laser spectra in the frequency range between $1930 - 1945 \text{ cm}^{-1}$. Some of the lines have been assigned to a combination band of C_4 , which allowed the frequency of the lowest bending vibration to be estimated. Further assignment is in progress.

RITZ ASSIGNMENT AND AWAT FIT OF THE RING-PUCKERING HOT BANDS OF OXETANE

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The oxetane molecule is the first oblate rotor to be investigated using the Ritz program. This molecule consists of 10 atoms, corresponding to 24 vibrational degrees of freedom. These include one large-amplitude vibration, i.e., the ring puckering, with its fundamental at approximately 53 cm^{-1} . The first rotationally resolved spectrum of these transitions has been reported recently, and a preliminary analysis of the first two bands has been presented^a.

We have investigated the oxetane spectrum between 52 and 162 cm^{-1} . Six different $\Delta v_{\text{rp}} = 1$ rotation-puckering transitions are observed in this region. The K_c selection rule for these transitions is $\Delta K_c = \text{even}$, and, practically, only $\Delta K_c = 0$ transitions are observed. This makes the spectrum not really suitable for a Ritz investigation since, for each $|v_{\text{rp}}, K_c; J\rangle$ energy level only the three downward transitions and the three upward transitions to $|v_{\text{rp}} - 1, K_c; J - 1/J/J + 1\rangle$ and $|v_{\text{rp}} + 1, K_c; J - 1/J/J + 1\rangle$, respectively, are observed. However, combining the Ritz with the Loomis-Wood procedure (which is included in the most recent version of the Ritz program), we could assign the transitions up to $v_{\text{rp}} = 5$. The first assignments of these higher ring-puckering bands have been presented in a previous conference^b. Here, some further improvements and refinements of the assignment procedure, will be presented.

The results of fitting our FIR data and previously published MW and MMW data with the AWAT1 program (Watson Hamiltonian for an asymmetric rotor, A-reduction, programmed by K. M. T. Yamada) for levels up to $v = 5$ will also be presented.

^aM. Winnewisser, M. Kunzmann and M. Lock, High Resolution FIR-Spectrum of Oxetane (Trimethylene Oxide): Analysis of the Ring-Puckering Fundamental Near 53 cm^{-1} and of Some Hot Bands, 53rd Ohio State University International Symposium on Molecular Spectroscopy, Columbus, June 15-19, 1998, TD04

^bG. Moruzzi, M. Kunzmann, B. P. Winnewisser and M. Winnewisser, Investigation of the Ring Puckering Hot bands of Oxetane by the Ritz Program, The 15th International Conference on High Resolution Molecular Spectroscopy, Prague, August 30 – September 3, 1998, H7

**PRECISION MEASUREMENTS OF ETHYLENE AND
ISOTOPIC ETHYLENE $^{13}\text{C}^{12}\text{CH}_4$ SPECTRAL LINES NEAR
10.5 μm BY THE INFRARED HETERODYNE
SPECTROMETER**

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In this report, we present initial results of laboratory investigations of absorption lines of ethylene C_2H_4 and isotopic ethylene $^{13}\text{C}^{12}\text{CH}_4$ in the ν_4 , ν_7 and ν_{10} bands near 10.5 μm by the Infrared Heterodyne Spectrometer with resolution $3 \times 10^{-5} \text{cm}^{-1}$.

The measurements were made at gas temperatures 293–297K and pressures 0.05–0.5 Torr. Positions of more than 200 absorption lines of C_2H_4 and $^{13}\text{C}^{12}\text{CH}_4$ were measured relative to lines in the P and R branches of the $^{12}\text{C}^{16}\text{O}_2$ laser and in the P branch of the $^{14}\text{C}^{16}\text{O}_2$ laser. Absolute frequencies and intensities of unblended strong lines were determined to better than $\pm 5 \times 10^{-5} \text{cm}^{-1}$ and $\approx 10\%$, respectively.

Self-broadening and foreign gas broadening coefficients of the $20_{11,10} \leftarrow 19_{10,9}$ (927.0188cm^{-1}) line in the ν_{10} band of C_2H_4 have been measured. Nitrogen (N_2) was used as the broadening gas. The measurements were made at gas temperature 295 K. The got value for self-broadening coefficient is $\gamma_{self} = 0.115 \text{cm}^{-1} \cdot \text{atm}^{-1}$ and for N_2 gas broadening coefficient is $\gamma_{\text{N}_2} = 0.076 \text{cm}^{-1} \cdot \text{atm}^{-1}$.

Authors acknowledge J.J.Hillman for help and very usable discussion.

**LINE MIXING IN IR SPECTRA OF INTEREST FOR
ATMOSPHERIC RADIATIVE TRANSFER**

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Line mixing occurs when rotationally inelastic collisions cause transitions among overlapping spectral lines. The results are an overall narrowing of the blended profile and lowering of the absorption in the wings of a vibration-rotation band. We have examined our laboratory spectra of CO₂ between 10 and 15 microns. We use an energy gap scaling law to determine the relaxation matrix elements to further compute the line mixing coefficients. Comparison of calculated and experimental spectra will be presented, showing the agreement we have reached, and that line mixing play a significant role in atmospheric radiative transfer, affecting the retrieval of atmospheric temperature profile.

**LINE BROADENING OF THE 551.5 GHz LINE OF NO
PERTURBED BY N₂ and O₂**

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In the purpose of remote sensing of atmospheric spectra planned to be observed by ODIN satellite, laboratory line broadening measurements have been performed on the 5.5-4.5 line of NO located near 551.5 GHz. The observed line consists of 3 hyperfine components (separated by about 2.5 MHz) of a Π doublet.

Experiments have been made at various temperatures in the 240-350K range by using a video-type spectrometer. This allows a direct comparison of the observed lineshapes with theoretical models.

Using Voigt profile lineshapes for the fit of observed spectra, discrepancies appear which cannot be explained even by the consideration of different broadening parameters for each component. Experimental lineshapes are well analysed by using a Galatry or Speed Dependent Voigt profile which take account of narrowing effects.

Retrieved relaxation parameters will be reported. In view of more specific lineshape studies, measurements with He, Ar and Xe as perturbers will be presented.

INVESTIGATION OF J -DEPENDANCE OF LINE BROADENING AND LINE SHIFT IN THE $\nu_1+3\nu_3$ BAND OF ACETYLENE PERTURBED BY He, Ne, Ar AND AIR

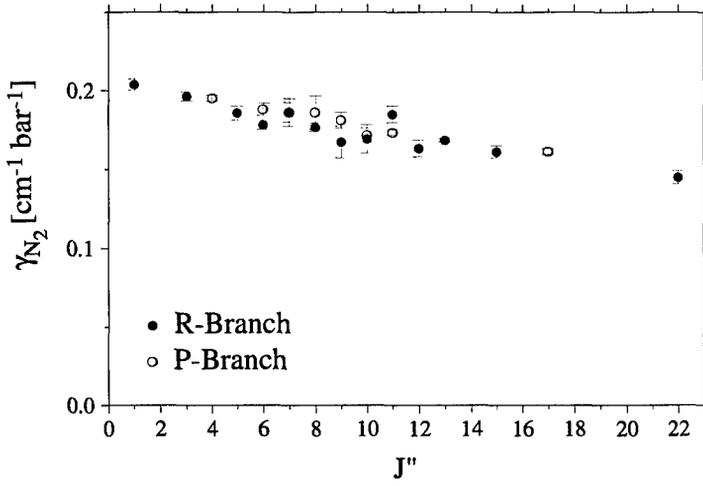
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Line shift and line broadening coefficients $\delta\nu$ and γ have been measured for 21 rotational lines of the P and R branch of the $\nu_1+3\nu_3$ band of acetylene at 789 nm using a multipass Herriot cell with an effective absorption length of 35 m. A tunable cw semiconductor laserdiode system was used as a light source providing about 20 mW power at the entrance window of the cell. Each single scan extended over a range of 0.8 cm^{-1} . The present paper contains our new results for broadening by He, Ne, Ar and air perturbers. Our previous results for self broadening and broadening by N_2 have already been published^a. Experiments studying the effect of Kr and of O_2 are presently in progress. In a first attempt we used a Voigt function to fit the experimental line profiles. However, we got better agreement between the experimental and the theoretical lineshapes by use of Galatry and Rautian functions, which take into account collisional narrowing effects. Using these functions we got slightly higher values of line broadening coefficients compared to those for a Voigt function. The broadening coefficients show a continuous decrease with increasing value of J , whereas the line shift coefficients show a clear increase. The results for line broadening and line shift coefficients are in good agreement with previous data for selected lines of the $\nu_1+3\nu_3$ band of acetylene of other authors^{b,c}. The line narrowing coefficient ζ of the Rautian varies between 1.2 bar^{-1} with a slight decrease for large values of J .

^aH. Valipour, D. Zimmermann, AIP Conf. Proc. 467, Spectral Line Shapes: Vol. 10, 14th ICSLS (1998), edited by Roger M. Herman

^bP. Cancio, F.S. Pavone, *Physica Scripta* T58, **86** (1995)

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Dependence of measured N_2 -broadening coefficients on the rotational quantum number J'' (Rautian profile)

ISOTOPOMER DEPENDENCE OF N₂- AND O₂-BROADENED HALFWIDTHS OF WATER VAPOR TRANSITIONS

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Pressure-broadened halfwidths are determined for the four most abundant isotopomers of water vapor in the terrestrial atmosphere. Nitrogen and oxygen are taken as the perturbing gases. Semi-classical calculations based on the Complex Robert-Bonamy (CRB) formalism [1] are made for transitions in the rotation and fundamental vibrational bands. The intermolecular potential is taken as a sum of the electrostatic contributions, an atom-atom potential expanded to 12th order and isotropic induction, and dispersion components [2,3]. The isotropic part of the atom-atom potential is fit to a Lennard-Jones 6-12 potential, which is used to define the dynamics of the collision process correct to second order in time. The pressure-broadened halfwidths for the different isotopomers are compared with each other and when possible compared with measurement.

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SELF-ASSOCIATION OF THE XANTHINE MOLECULES AS STUDIED BY FTIR SPECTROSCOPY, FACTOR ANALYSIS AND SEMIEMPIRICAL QUANTUM MECHANICS

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In order to study the self-association of the amino acid xanthine in carbon tetrachloride, evolving factor analysis was applied to the Fourier transform infrared spectra of xanthine solutions with different concentrations of the solute. The results indicate that the xanthine molecules could exist in up to seven self-associated dimer forms. In order to obtain an insight into the relative thermodynamic stability as well as the frequencies of the individual self-associated dimer forms in the N-H and C=O stretching regions, AM1 semiempirical quantum mechanical calculations were performed. The obtained frequencies were used as input parameters for curve fitting of the experimental Fourier transform infrared spectra in the regions where the corresponding bands of the dimers appear. The results show that factor analysis in combination with semiempirical quantum mechanical calculations and curve fitting can be successfully used in the study of the self-association of xanthine molecules and, possibly, of other types of molecules which could exist in more than one self-associated dimer form.

A COMPACT MILLIMETER WAVE SPECTROMETER IN THE 50 - 110 GHz REGION

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The spectroscopy group at the RWTH Aachen has recently developed a millimeter wave spectrometer for rotational spectroscopy on static gases and molecular beams. This supplements two molecular beam FT microwave spectrometers in the 3.0-26.5 GHz and 26.5 - 40.0 GHz ranges which are not suitable to study high rovibrational states.

The millimeter wave spectrometer is operated in a conventional absorption mode using frequency modulation and $2f$ phase sensitive detection of the signal received by Schottky diode detectors. A microwave synthesizer (HP83624B) up to 20 GHz with two active multipliers (factor 4 for the 50 to 75 GHz range and factor 6 for the 75 to 110 GHz range) is used as a millimeter wave source.

An important aspect is the usage of the internal frequency modulation circuit of the synthesizer at a modulation frequency of 15 kHz. Usually at such a low frequency the PLL of the synthesizer tries to compensate the modulation signal. Therefore, the manufacturer recommends to turn it off, while otherwise a distorted modulation will result or the PLL will not work at all. On the other hand we found that in this mode the resulting frequency accuracy is no longer suitable for high resolution spectroscopy. For high modulation frequencies (> 100 kHz) the PLL is not fast enough for regulation and the microwave signal remains accurate. We decided to operate the synthesizer far beyond the specifications and used the PLL even at 15 kHz modulation frequency. Surprisingly, this works well for a small modulation depth as needed for spectroscopy and it is very important for using a synthesizer at all.

Technical details of the spectrometer and some sample spectra showing sensitivity and resolution will be presented. The spectrometer has been used for investigation of dimethyl sulfone $(CH_3)_2SO_2$ and sulfuranyl fluoride SO_2F_2 . Some broad band scans, as well as some spectra of isotopomers and transitions in vibrationally excited states will also be presented.

ANALYSIS OF THE OCTAD SYSTEM OF $^{12}\text{CH}_4$

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In view of planetary applications, the middle infrared spectrum of methane has been investigated. In the spectral range ($3500 - 4700 \text{ cm}^{-1}$), there are eight bands ($3\nu_4$, $\nu_1 + \nu_2$, $\nu_1 + \nu_4$, $\nu_2 + \nu_3$, $\nu_3 + \nu_4$, $2\nu_2 + \nu_4$, $\nu_2 + 2\nu_4$, and $3\nu_2$), and only three of them, namely $\nu_2 + \nu_3$, $\nu_1 + \nu_4$, and $\nu_3 + \nu_4$ had been analyzed (separately). The challenge of the present work is to analyze all eight bands in a polyad scheme.

The theoretical background for modelling vibration-rotation energy levels and corresponding transitions has been reviewed recently^a. For the octad, the Hamiltonian operator can be written as

$$\tilde{H}^{\langle \text{Octad} \rangle} = \tilde{H}_{[\text{Ground}]}^{\langle \text{Octad} \rangle} + \tilde{H}_{[\text{Dyad}]}^{\langle \text{Octad} \rangle} + \tilde{H}_{[\text{Pentad}]}^{\langle \text{Octad} \rangle} + \tilde{H}_{[\text{Octad}]}^{\langle \text{Octad} \rangle}. \quad (1)$$

Each term is a linear combination of rovibrational operators, the number of which depends on the chosen order of approximation. The 206 parameters of the first three terms of H have been fixed to the values resulting from the analysis of the lowest polyads : the ground-state and the dyad to sixth order^b and the pentad^c to fourth order with (10+62+134) parameters. For the specific octad part of H, a model has been used with all 253 second-, third- and fourth-order parameters.

The main experimental data are a number of F.T. spectra recorded at Keat Peak National Observatory with different pressures (1 to 10 Torr) and lengths (1.5 to 12 m) for the octad range, and $p = 3$ Torr and $l = 24, 192, 432$ m for the hot bands. A spectrum of the whole octad recorded at 193 K is also used to help J identification of lines. As a complement, we use spectra of the

^aJ.-P. CHAMPION, M. LOETE AND G. PIERRE, *Spectroscopy of the Earth's Atmosphere and Interstellar Medium : Spherical Top Spectra*, Academic Press Inc., U.S.A., (1990).

^bC. ROCHE AND J.-P. CHAMPION, *Can. J. Phys.*, **69**, 40, (1991).

^cJ.-C. HILICO, J.-P. CHAMPION, S. TOUMI, G. TYUTEREV AND S. A. TASHKUN, *J. Mol. Spectrosc.* **168**, 455, (1994).

Q-branches regions of $3\nu_4$, $\nu_2 + 2\nu_4$, $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ obtained by A.S. Pine (at N.I.S.T.) at 80 K and 296 K. In this case, absorbances were measured and J was experimentally determined.

At the present step, the analysis of the complete octad has been performed for $J \leq 16$ with a Hamiltonian containing 253 adjustable parameters (for 8 bands and 24 subbands). Near 8000 lines in the octad have been assigned. They are reproduced with a standard deviation of 0.044 cm^{-1} .

The present simultaneous analysis of the eight bands appearing in the $2.2 - 2.8 \mu\text{m}$ spectral range includes the first identification of the bands $3\nu_4$, $\nu_2 + 2\nu_4$, $2\nu_2 + \nu_4$, $3\nu_2$ and the quasi-dark band $\nu_1 + \nu_2$. The first calculations of the upper-polyad energy levels are in progress.

THE SET OF VALLEY RIDGE INFLECTION POINTS ON THE POTENTIAL ENERGY SURFACE OF WATER

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The MP2/6-31G** potential energy surface (PES) of the water molecule is used to follow the reaction paths (RP) of "inversion" and dissociation and their possible bifurcations by steepest descent, reduced gradient and global Newton methods. The PES analysis is illustrated by using surface sections as well as curves lying in the three-dimensional coordinate space. The recently proposed reduced gradient following method gives curves, which we may interpret to be possible reaction path approximations. We calculate curves of valley ridge inflection (VRI) points in the configuration space. Crossing points between VRI curves and RP (approximations) allow to identify symmetrical bifurcation of RP. The recently obtained results for a model PES^a are confirmed by using a real molecule. The possible chemical and physical meaning of the VRI curves is discussed including other H₂X molecules and the 4-fold cluster problem of high rotational states.

^aW. Quapp, D. Hirsch, D. Heidrich, *Theor. Chem. Acc.* 100, 285 (1998).

HIGH-RESOLUTION MEASUREMENTS OF LINE AND BAND OS STRENGTHS IN THE DIPOLE-ALLOWED ABSORPTION SPECTRUM OF $^{14}\text{N}_2$

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We have completed a long series of high-resolution experiments directed at systematically measuring the line and band oscillator strengths in the absorption spectrum of $^{14}\text{N}_2$ from 99.4 to 66.5 nm. At the longest wavelengths, the experiments at the Photon Factory synchrotron facility in Tsukuba (Japan) have been carried out at room temperature under precisely known equilibrium conditions. At shorter wavelengths, most of the measurements were made on supersonic jet expansions, cooling the absorbers to rotational temperatures of 30 K and greatly reducing the overlap of adjacent band structures. The absorption measurements are compatible with low-resolution electron scattering results,^a providing, however, a far more detailed picture of the oscillator strength distribution at near-threshold energies.

^aW. F. Chan, G. Cooper, R. N. S. Sodhi, and C. E. Brion, *Chem. Phys.* 170, 81 (1993).

THE INFLUENCE OF AN EXTERNAL MAGNETIC FIELD ON THE SCATTERING LENGTH OF Na

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In a molecular beam experiment starting with thermally populated molecular ground state levels we apply Franck-Condon pumping followed by a coherent process to access the last bound levels of the $X^1\Sigma_g^+$ ground state of Na₂. In contrast to photoassociation, this method is able to resolve the hyperfine structure of single rotational levels. We observe typical linewidths of 15 MHz. With this experiment, we were able to observe the last bound levels near the asymptotes and to determine with high precision the scattering lengths [1,2]. The excellent resolution of the experiment allows to investigate the influence of external fields on the level positions. Recently, we applied a magnetic field to study the Zeeman effect. We observe with good S/N the shift and the splitting of the singlet levels, and we see lines due to certain triplet levels appearing at elevated magnetic fields.

By the magnetic field the scattering lengths are modified. Thus the present experiment will reveal highly precise data on the manipulation of the scattering lengths by magnetic fields. Such data are applicable to describe the formation and dynamics of Bose-Einstein condensates under external fields. The present status of the investigations will be reported.

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LIFETIMES OF THE LOWEST ELECTRONICALLY EXCITED STATES 3A_2 AND 3B_2 OF OZONE

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High resolution absorption spectra (0.014 cm^{-1}) of ozone have been recorded using Intra-Cavity-Laser-Absorption-Spectroscopy (ICLAS) in the near infrared spectral range at around $1\mu\text{m}$. The rotational analysis, taking into account spin rotation and spin spin coupling for the singlet triplet transitions, confirm the 3A_2 and 3B_2 state to be the upper states in the observed spectra. The ozone molecule shows case B coupling behaviour and the obtained molecular parameters are close to predictions from ab initio calculations. The assignment of single resolved rovibrational lines has been possible in the least congested region of the 3A_2 (000) and 3A_2 (010) vibrational bands. These lines show variation of their linewidths depending upon the J and K rotational quantum number. The short lifetimes inferred from these linewidths suggest that none of these triplet states is metastable nor long lived. This rotational induced predissociation is attributed to a perturber state, which is most likely the electronic ground state 1A_1 . The impact of these results on the recombination kinetics of ozone, heavy isotope enrichment, photochemistry and the atmospheric chemistry will be discussed.

**ISOMERS AND MICROSOLVATION IN $\text{SiOH}^+\text{-Ar}_n$
COMPLEXES (n=1-10)**

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Infrared photodissociation spectra of mass selected $\text{SiOH}^+\text{-Ar}_n$ ionic complexes have been recorded in the vicinity of the OH stretch vibration in a tandem mass spectrometer. Two isomers are identified in the spectrum of the dimer (n=1) via rotational and vibrational analysis and comparison with ab initio calculations: a linear proton bound dimer and a T-shaped complex. Though the spectra of larger clusters (n=2-10) display only vibrational resolution, the analysis of the systematic complexation induced frequency shifts provides a detailed picture of the cluster growth, including the formation of solvation rings and the existence of various isomers.

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF THE WEAKLY BOUND DIMER N₂-IH

WOLFGANG JABS, AVERY McINTOSH, ROBERT R.

LUCCHESI, JOHN W. BEVAN, *Chemistry Department, Texas A&M University, College Station, Texas, 77843*; **RICHARD D. SUENRAM**, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899*

The pulsed nozzle Fourier transform microwave spectrum of ¹⁴N₂:HI has been recorded in the frequency range 12–17.1 GHz. The hyperfine pattern of the observed transitions are not only complicated by the quadrupole moments of ¹²⁷I and ¹⁴N but also by doubling of about 4 MHz caused by internal rotation of the N₂ moiety. A total of 78 transitions occurring in two tunneling states could be assigned and fitted to a Hamiltonian suitable for a linear molecule. The recorded spectrum of the adjacent transitions $J : 5 \leftarrow 4, 6 \leftarrow 5$ and $7 \leftarrow 6$ were found to be consistent with a N₂-I-H isomeric ground state with $R_{\text{cm}} = 4.20 \text{ \AA}$, $\theta = 25.6^\circ$ and $\phi = 156.2^\circ$, where θ denotes the oscillation angle of the N₂ moiety and ϕ the oscillation angle of the HI moiety. These results demonstrate that the ground state structure of N₂-IH differs from the corresponding structures of other members of the homologous series N₂-HX (X=F,Cl,Br). The determined structural parameters will also be compared with corresponding results predicted on the basis of *ab-initio* calculations.

SLIT JET INFRARED ABSORPTION SPECTROSCOPY OF $C_2H_2 - HCl$ COMPLEXES

P. CARCABAL, M. CHEVALIER, M. BROQUIER and A. PICARD-BERSELLINI, *Laboratoire de Photophysique Moléculaire CNRS, Université Paris-Sud, 91405 Orsay, France*

The vibration-rotation spectra of the weakly bound complexes $C_2H_2 - HCl$ have been studied in the $3.5\mu m$ region of the ν_1 fundamental band correlated with the HCl stretch, by means of a pulsed slit jet expansion and a tunable diode laser spectrometer. For the first time the ν_1 band for $C_2H_2 - H^{35}Cl$ and the $C_2H_2 - H^{37}Cl$ isotope has been observed. The rotational structure of the bands exhibits a A-type behaviour, pointing out that the HCl lies on the a-inertial axis of the complex. This fact agrees with the T-shape geometry of the complex already deduced by Legon et al. in the microwave study [J. Chem. Phys., **75**(2), p 625 (1981)]. The spectra of both isotopes have been analysed. The assigned lines frequencies were fitted with the Watson Hamiltonian in the A-reduction and the vibrational shifts and the rotational constants A, B, C, D_{JK} and D_{JJ} were determined for the fundamental and the first excited vibrational states. Their values are listed in cm^{-1} below:

- for $C_2H_2 - H^{35}Cl$:

fundamental vibrational state: $A''=1.2002$; $B''= 0.0827$; $C''= 0.0770$;

$D_{JK}''=0.165D-04$; $D_{JJ}''=0.264D-06$;

first excited vibrational state: $A'=1.1976$; $B'= 0.0839$; $C'= 0.0780$;

$D_{JK}'=0.133D-04$; $D_{JJ}'=0.322D-06$;

origin band frequency= 2806.9175 ; vibrational shift= -79.0602 ;

- for $C_2H_2 - H^{37}Cl$:

fundamental vibrational state: $A''=1.1998$; $B''= 0.0808$; $C''= 0.0753$;

$D_{JK}''=0.158D-04$; $D_{JJ}''=0.254D-06$;

first excited vibrational state: $A'=1.1975$; $B'= 0.0819$; $C'= 0.0763$;

$D_{JK}'=0.836D-05$; $D_{JJ}'=0.230D-06$;

origin band frequency= 2804.8413 ; vibrational shift= -79.0295 ;

THE ELECTRONIC STATES OF THE FeH RADICAL : A PROGRESS REPORT

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The electronic spectrum of the FeH radical in the visible region has been studied using the techniques of laser excitation spectroscopy and dispersed fluorescence ^{a,b}. We have recently made good progress in the definition and understanding of the low-lying states below 5000 cm⁻¹. In particular, the lowest three spin-orbit components of the b⁶Π state have been identified together with the lowest spin component of C⁴Φ state (Ω = 7/2). As a result, all three of the expected low-lying sextet states have now been located. Some other sets of rotational terms have also been identified but it has not yet proved possible to assign them to particular electronic states. The investigation of hot bands in a particularly rich region of the electronic spectrum of FeH from 525 to 545 nm has enabled us to characterize the excited vibrational level (v = 1) of the e⁶Π state at about 22 400 cm⁻¹ which gives a vibrational interval of about 1715 cm⁻¹ in this state. Remarkably few of the hot band transitions assigned could be identified in the high temperature spectrum of FeH recorded by McCormack and O'Connor ^c. Therefore there remains some mystery as to the nature of the many unassigned lines in this congested region of both the high and ambient temperature spectra.

^aD. M. Goodridge, R. T. Carter, J. M. Brown and T. C. Steimle, *J. Chem. Phys.*, **106**, 4823 (1997)

^bD. M. Goodridge, D. F. Hullah and J. M. Brown, *J. Chem. Phys.*, **108**, 428 (1998)

^cP. McCormack and S. O'Connor, *Astron. Astrophys. Suppl.*, **26**, 373 (1976)

FOURIER TRANSFORM EMISSION SPECTRUM OF THE ELECTRONIC C³Π - X³Π TRANSITION OF THE SiC RADICAL

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The emission band system of the C³Π - X³Π transition of the SiC radical, previously detected by LIF studies [1,2] was recorded by means of Fourier Transform spectrometry with a 0.1 cm⁻¹ resolution.

A D.C. discharge through a flowing mixture of helium and hexamethyldisilane (trace) turned out to be a good reproducible source for the production of the SiC radical. Two electronic transitions belonging to the SiC radical could be identified in the emission spectra: the d¹Σ⁺ - b¹Π transition at 6100 cm⁻¹ and the C³Π - X³Π in the violet region.

Although quite weak and especially, strongly overlapped by emissions from other species, the analysis of three bands: 2-0, 3-0, 4-0 allowed us to obtain more precise molecular constants for the C³Π state. Furthermore, the better calibration and higher resolution of the Fourier Transform spectra altogether with the observation of higher rotational numbers J, made possible the determination for the first time of the spin interaction constants: λ, λ_D, γ of the same electronic state.

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 2. T. J. Buttenhoff, E. A. Rohlfing, J. Chem. Phys. **95**(6), p 3939 (1991)

**A CONTINUED FRACTION EXPANSION OF THE
BORN-OPPENHEIMER POTENTIAL ENERGY FUNCTION
FOR DIATOMIC MOLECULES**

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Expansion of the internuclear Born-Oppenheimer potential for diatomic systems, in the form of a continued fraction has been investigated.^a This function satisfies all criteria applicable to a real potential curve of molecules in a stable electronic state; it asymptotically approaches a finite value in the dissociation limit, exhibits a minimum energy at the equilibrium internuclear separation, and approaches positive value greater than a dissociation energy as the separation decreases. The proposed expansion is applied in quantitative analysis of the infrared, microwave and Raman spectra of BrCl, NaCl and N₂. The observed transitions are reproduced within experimental errors by making use of fewer fitted parameters than in the approach which employs a power expansion of the potential energy function.

^aM. Molski *Phys. Rev. A* (1999). To be published

PREDICTION OF PREDISSOCIATION EFFECTS IN THE $0_u^+(^2P_{3/2})$ STATE OF Rb_2 AND Cs_2 , USING THE MAPPED FOURIER GRID HAMILTONIAN METHOD

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The [$A^1\Sigma_u^+(0_u^+) \sim b^3\Pi_u(0_u^+)$] pair of excited electronic states in alkali dimers, coupled through spin-orbit interaction, is a well-known example of perturbations between molecular states [1]. For the heavier alkali dimers (Rb_2 and Cs_2), the corresponding fluorescence spectra has been recently studied by Fourier Transform Spectroscopy, which has revealed very strong mixing between the two states ([2], and poster by C. Amiot et al).

In the present contribution, we propose a theoretical study of the perturbations for the vibrational levels close to the first excited dissociation limit $S + ^2P_{1/2}$. We are also considering the predissociation for the vibrational levels located between the $S + ^2P_{1/2}$ and $S + ^2P_{3/2}$ dissociation limits. We use the recently developed Mapped Fourier Grid Hamiltonian method [3] which has been demonstrated to be very efficient for long-range bound levels. Lifetimes of the predissociated levels are also computed, exhibiting a strong isotopic effect in the case of Rubidium. The comparison with experiments is discussed, especially in the direction of the photoassociation spectroscopy in cold atom traps [4].

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[4] R.A. Cline, J. D. Miller and D. J. Heinzen Phys. Rev. Lett., **73**,632 (1994). C.D. Wallace, T.P. Dinneen, K.Y.N. Tan, T.T. Grove, and P.L. Gould, Phys. Rev. Lett. **69**(6), 897-900 (1992).

SURFACE AND BULK DIFFUSION OF ATMOSPHERIC GASES ON ICE INVESTIGATED BY RESONANT INFRARED LASER DESORPTION / REMPI MASS SPECTROMETRY

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In spite of the great importance for atmospheric chemistry of chemical and physical processes occurring at the gas-ice interface, there are currently few available experimental techniques for direct study of the diffusion of gases in ice or heterogeneous reactions occurring on its surface. As a matter of fact, surface and bulk diffusion coefficients have been characterized only for some simple inorganic chemical species (HCl, HNO₃, ...) ^a. There is thus a growing interest in efficient micro-probing methods for selective, ultra-sensitive detection of specific chemical species, including organic molecules, trapped in ice ^b.

We are developing a two-step laser resonant desorption-ionization technique ^c for the detection of trace molecules in collaboration with the "Laboratoire de Glaciologie et Géophysique de l'environnement" (LGGE-Grenoble). A first pulsed OPO laser with $l = 3.1$ mm is used for resonant desorption of the ice surface. A second tunable dye laser with $l = 220 - 600$ nm resonantly ionizes neutral molecules released from the frozen matrix. Photo-ions are detected by a Time-Of-Flight (TOF) mass spectrometer.

The combination of laser resonant desorption (MALD), resonant photo-ionization (REMPI) and mass spectrometry provides high selectivity and sensitivity with good spatial resolution in the volume of the ice sample. A detailed description of the experimental setup as well as preliminary results will be presented.

^aF. Livingston and S. George, *J. Phys. Chem.*, **102**, 10280 (1998).

^bE. Thibert and F. Dominé, *J. Phys. Chem. B*, **101**, 3554 (1997).

^cS. Alimpiev, M. Belov, V. Milinsky and S. Nikiforov, *Analyst*, **119**, 579 (1994).

Invited Lectures G

Tuesday, September 7, 14:00

Chairman : P. JENSEN

NON LINEAR VIBRATIONAL SPECTROSCOPY OF MOLECULES IN SOLIDS AND AT SURFACES

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Non linear interactions of laser fields with matter provide powerful spectroscopic tools for the understanding of dynamical processes and intermolecular interactions in molecular systems. Second and third order non linear optical techniques such as second harmonic generation (SHG) infrared-visible sum frequency generation (SFG), degenerate four wave mixing as well as pump-probe and hole burning techniques have been widely employed in spectroscopy of molecules in the gas phase, in clusters, in matrices and in restricted geometries (e.g. surface monolayers or zeolites). However the development of non linear vibrational spectroscopy has suffered from the lack of appropriate laser sources. Recent advances in IR free electron lasers and optical parametric oscillators and amplifiers have considerably boosted the application of non linear techniques to the vibrational spectroscopy of molecules dispersed in solid matrices or adsorbed onto surfaces. Recent work involving IR picosecond pump-probe and photon echoes experiments on several prototypical systems such as $W(CO)_6$ and CO molecules in various solid environments (e.g. rare gas matrices, organic glasses, xerogels, fullerenes, metal surfaces) as well as picosecond or femtosecond SHG or SFG studies will be reviewed.

SINGLE, DOUBLE AND TRIPLE TRANSITIONS IN THE ROVIBRATIONAL SPECTRUM OF SOLID H₂, D₂ AND HD

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The study of solid hydrogen using FTIR in combination with a long sample path length has led to new types of transitions and an extended understanding of the interactions responsible for the spectrum. Our initial measurements of H₂ have been supplemented by measurements of D₂ and HD, and by at least one measurement of the liquid of each species.

Earlier measurements carried out in our laboratory covered the fundamental band and the first overtone band of hydrogen, that is 3000–8500 cm⁻¹. Our latest measurements extend from that region down to 600 cm⁻¹ and up to 16 500 cm⁻¹, thus including part of the pure rotational spectrum and the second overtone region. Two different methods of extending the sample path were used: a White-type cell with multi-pass mirrors external to the sample cryostat, and a cell inside the cryostat for which spherical mirrors, each with a small optical aperture, serve as window elements.

The observed transitions include single-molecule transitions with $\Delta J = 0, 2, 4, 6$ and 8 . Double transitions, in which two individual molecules are simultaneously excited, actually dominate the spectrum. These all have different widths, with various types of structure, and all show in addition satellite structure due to ortho-H₂ impurity molecules. Each of the observed line shapes can be qualitatively accounted for with established pair-interaction theory, although quantitatively our current results indicate some incompleteness of the models.

Triple transitions, in which one photon excites three molecules simultaneously, had been predicted but expected to be very weak in solid H₂. We found two new categories of triple transitions which are stronger and much easier to observe than expected. Calculations of the intensities and structure of these transitions led to full agreement with the observations. The observations in the spectra of D₂ and HD have been used so far primarily to confirm these observations of triple transitions.

Poster Session H
Tuesday, September 7, 16:00

**DIRECT TWO PHOTON TRANSITIONS IN HIGH
FREQUENCY ELECTRON PARAMAGNETIC RESONANCE
DESCRIBED BY A 3-LEVEL DENSITY MATRIX FORMALISM**

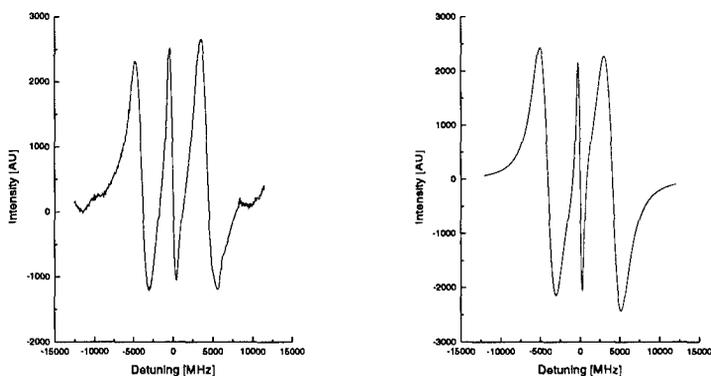
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High frequency EPR spectroscopy is a powerful tool for revealing the magnetic resonance properties of Nickel(II) complexes with an $S=1$ (triplet) ground state. For $\text{Ni}(\text{ethylenediamine})_3(\text{NO}_3)_2$ we observed first-order spectra at 95 GHz. A single crystal of this compound shows two *normal* $M_S = 0 \leftarrow M_S = 1$ and the $M_S = -1 \leftarrow M_S = 0$ transitions with an effective zero-field splitting depending on the orientation in the magnetic field. Moreover, a direct transition that corresponds to $M_S = 1 \leftarrow M_S = -1$ is observed. For this transition, the intensity is strongly orientation dependent. At the magic angle all three transitions fall on top of each other for this axially symmetric crystal. All three transitions show the same dependence on microwave power. The existence of the $\Delta M_S = 2$ and its dependence of the microwave power cannot be understood and explained in a (conventionally used) 2-level picture of each transition in a triplet system.

In the present work we present the results of a 3-level density matrix calculation. This fully explains the observed phenomena. The calculation starts from the general equation of motion of the density matrix operator in the Heisenberg picture^a.

^aN. Dam, Ethylene Hot-band Spectroscopy and Relaxation phenomena, Thesis 1988, University of Nijmegen.

In addition we incorporate the diagonal AC Zeeman effect. This leads to allowed multiphoton transitions without the presence of any intermediate level(s) at surprisingly low AC field strengths. This effect has its analog to the multiphoton transitions discussed in the 2-level Stark transitions observed in molecular beam electric resonance experiments^b.



Experimental(left) and calculated spectrum for an angle between the magnetic field and the crystal axis of 69.8° .

^bW.L. Meerts, J.T. Hougen and I. Ozier, *J. Chem. Phys.* 90 (1989) 4681-4688.

HIGHLY-SENSITIVE DETECTION OF METHANE IN AIR BY DIODE-PUMPED, MID-INFRARED, DIFFERENCE-FREQUENCY GENERATION IN QUASI-PHASE-MATCHED LiNbO₃

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LEO HOLLBERG, *Time and Frequency Division, National Institute of
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Precise measurements on isotopic fractionation of atmospheric species is useful in determining their sources and sinks. A compact and highly sensitive mid-infrared spectrometer based on difference-frequency-generation in periodically poled LiNbO₃ (crystal length = 20 mm, used at normal incidence) has been constructed for this purpose; particular interest is in naturally occurring methane and nitrous oxide in air samples. An α -DFB laser^c operating at 550 mW provides the signal power and a conventional Fabry-Perot diode laser operating at 70 mW provides the pump power to generate broadly tunable difference-frequency radiation at the 10- μ W level (efficiency = 0.013%·W⁻¹·cm⁻¹) in the 3.35- μ m to 3.41- μ m region. The mid-IR radiation probes gas samples in a 36-m pathlength, multipass cell (volume = 0.3 l, optical throughput = 17%), and the emerging optical power is detected by an InSb photovoltaic detector, operating at 77 K (detector area = 1 × 1 mm², noise equivalent power \approx 0.5 pW·Hz^{-1/2}). Wavelength modulation is employed to improve the signal-to-noise ratio, and a lock-in amplifier records the resulting 2-f absorption spectrum.

In order to investigate the usefulness of this spectrometer for measuring isotopic fractionation of atmospheric species, we acquired Doppler-limited spectra of methane in natural air samples provided by the Climate Monitoring and Diagnostics Laboratory of the National Oceanic and Atmospheric Administration (NOAA/CMDL), containing a calibrated mixing ratio of 1.7 ppm for methane. Our measurements demonstrate a detection limit of 4 × 10⁹ molecules·cm⁻³ (1 Hz bandwidth) for methane lines with extinction coefficients of 1 × 10⁻¹⁹cm·molecule⁻¹. The detection limit is currently limited by residual fringes arising from optical standing-waves in the multipass cell. A concurrent effort by collaborators at NOAA/CMDL and the University of Colorado is taking place to extract methane from 50 l of air sample (collected globally by NOAA/CMDL Cooperative Air Sampling Network) at a time.

^aGuilherme de Andrade Garcia is funded by FAPESP Brasil

^cG. de Andrade Garcia and L. Hollberg, *Conference Digest, 1998 IEEE 16th International Semiconductor Laser Conference*, pp. 249-250.

This will provide a CH_3D concentration of 4×10^{12} molecules \cdot cm $^{-3}$, enabling fractionation measurements with per-mil precision, or better, for CH_3D and $^{13}CH_4$ in the atmosphere. In addition, various measures will be taken to further reduce fringes and to stabilize the infrared power to reach detector-limited spectrometer sensitivity (we are currently ~ 300 times above the detector-noise limit).

**CONSTRUCTION OF A THREE-DIODE-LASER,
TERAHERTZ, DIFFERENCE-FREQUENCY SYNTHESIZER
AND ITS APPLICATIONS TOWARD SPECTROSCOPY OF
AMMONIA IN THE ν_2 STATE AND WATER IN THE
GROUND AND ν_2 STATES**

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An all-solid-state, high-resolution and frequency-calibrated THz spectrometer based on optical heterodyne in low-temperature-grown (LTG) GaAs has been constructed.^a This setup utilizes three distributed-Bragg-reflector (DBR) diode lasers to generate accurate and tunable difference-frequencies in the THz regime. Lasers #1 and #2 are locked to different longitudinal modes of an ultra-low-expansion Fabry-Perot etalon, and laser #3 is offset locked to laser #2, where the offset frequency (ν_{offset}) is set by a microwave sweeper. This three-laser, difference-frequency synthesizer is fully fiber coupled in rigid and compact optical rails. The primary outputs of lasers #1 and #3 pump the LTG GaAs photomixer to generate THz radiation (whose frequency equals to $n \times FSR + \nu_{offset}$, where FSR is the free spectral range of the etalon and n is an integer). The etalon's FSR , and thus, the THz frequency, has been calibrated to 50 ppb by acquiring spectra of the 10 rotational lines of CO in the 0.23 to 1.6 THz region.

Using this spectrometer, we obtained measurements of 26 pure inversion and inversion-rotation transitions of ν_2 -NH₃ at an accuracy significantly higher than previously published values. In addition, 17 new measurements of H₂O transitions in the ground and ν_2 states have been acquired. In this paper, we discuss the design, frequency calibration, and the calibration stability of the spectrometer. Spectroscopic results (frequency measurements and fitted molecular parameters) will be presented as well.

^aShuji Matsuura, Pin Chen, Geoffrey A. Blake, John C. Pearson and Herbert M. Pickett, *IEEE MTT*, in press (1999).

**THEORETICAL STUDY OF TWO-PHOTON ABOVE
THRESHOLD DISSOCIATION AND RELATED PROCESSES
IN ALKALI MOLECULAR IONS**

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With the development of ultra-short and intense pulse lasers, photodissociation and photoionization of small alkali dimers may be observed in future. In contrast with the molecules for which probabilities of multiphotonic dissociation are difficult to predict due to the competition between ionization and fragmentation processes, multiphotonic dissociation of molecular alkali ions seems to be easier to perform. Recently we have proposed a theoretical study of the above threshold dissociation ATD of the cations of the dimers of Li and of Na, where the molecular ion even after reaching the lowest dissociative continuum, can absorb photons and make continuum-to-continuum transitions before dissociating. Basically, we have considered several processes from the analysis of molecular potential curves and relevant transition dipole moments. Simulations of photodissociation spectra are based on quantum wavepacket propagation. We have established the best conditions to observe such a process and suggested two-color experiments easily feasible with moderately high laser intensities. In particular, we have demonstrated for the first time, the occurrence of Rabi oscillations between continuum states and radiation-molecule interference.

VIBRATIONAL RELAXATION AND HOT LUMINESCENCE OF SELF-TRAPPED EXCITONS IN ATOMIC CRYOCRYSTALS

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Self-trapped excitons (STE) in atomic cryocrystals (Xe, Kr, Ar, Ne) represent quasimolecular centres, which are in many respects similar to diatomic rare gas excimers (R_2^*). We have studied, both experimentally and theoretically, vibrational relaxation and hot luminescence of STE in solid Xe and Kr. The crystals (usually of volume 2-3 cm³) were grown from the liquid in a He cryostat near the triple point under near-equilibrium conditions ^a. X-ray excitation through a Be window and two-photon ArF and KrF excimer laser excitation were used in luminescence experiments. The emission spectra have been recorded with the help of a double vacuum monochromator.

Theoretical treatment was based on a new nonperturbative approach ^b, which predicts abrupt acceleration of relaxation near characteristic amplitudes of strong local vibration. A step-wise increase of the two- and three-phonon decay was indeed found for the centre Xe_2^* in solid Xe. Fully quantum-mechanical calculation of the hot luminescence spectrum has been performed, based on the analytical method by one of the authors ^c. Quantum-mechanical Franck-Condon factors have been normalized in accordance with the fundamental demand of completeness of the system of energy eigenfunctions, taking account of all quantum transitions in the discrete and continuous spectrum of the electronic states under examination.

Research has been supported by Estonian Science Foundation Grants No. 2274, 2689 and 3455.

^a M. Kink, R. Kink, V. Kisand, J. Maksimov, M. Selg, *Nucl. Instr. and Meth. in Phys. Research B* **122**, 668-676 (1997).

^b V. Hizhnyakov, *Europhysics Letters* **45**, 508-513 (1999).

^c M. Selg, *Exactly Solvable Modified Morse Potentials for Quantum-Mechanical Applications*, *Physica Scripta* (accepted for publication).

**IONIC MOTIONS AND PHASE TRANSITIONS OF
 $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ STUDIED BY ^1H NMR**

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The motions of the planar diaquahydrogen ion H_5O_2^+ in crystalline $\text{H}_3\text{P}-\text{W}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ are studied by ^1H NMR second moment (M_2) and spin-lattice relaxation time (T_1) measurements. Comparison of the experimental values and theoretical calculation suggests that the pseudo- C_4 reorientation around central H^+ occurs at 140 K and $\text{H}_3\text{O}^+-\text{H}_2\text{O}$ behavior appears at temperatures higher than 315 K. The phase transitions were observed at 143 and 313 K by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The enthalpy change and the T_1 minimum value show that the order-disorder phase transition at 143 K occurs from the state having a single potential well to another having unequal potential wells. These analyses are presented.

UV LASER SPECTROSCOPY USING THE VELOCITY MODULATION TECHNIQUE : STUDY OF A $\text{SiCl}_4/\text{O}_2/\text{He}$ DISCHARGE AROUND 325 NM

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The dry etching processes of semiconductors using chlorine-based gases have been extensively studied during the last decade ^a. SiCl_4 has been proven effective in etching III-IV compounds for patterning small structures. The etching processes were studied by low resolution emission spectroscopy of SiCl_4 plasmas. Signals belonging to molecular species like SiCl , SiCl_2 , Cl_2 , and Cl_2^+ have been identified. In particular it was found that the principal etchant for polycrystalline silicon was Cl_2^+ . Meanwhile the near UV region is not very well characterised and motivated the present study.

Our new cw UV laser spectrometer dedicated to the high resolution spectroscopy of molecular ions has been used. It has fully been described in a recent paper ^b. We have studied the positive column of an ac ($f = 43$ kHz) glow discharge of a SiCl_4/He cold plasma, with a current of 300 mA peak-to-peak giving a voltage of 4 kV peak-to-peak. Several signals have been detected in the region around 325 nm. The signal-to-noise ratio of most ion signals was then optimised in a $\text{SiCl}_4/\text{O}_2/\text{He}$ gas mixture discharge with a ratio of 1/1/15 respectively at a downstream total pressure of 15 torrs.

By replacing SiCl_4 by TiCl_4 in the gas mixture the same signals were observed. It strongly suggested that they could belong to a band system of Cl_2^+ . This molecular ion is not well characterized. The visible $A^2\Pi_u - X^2\Pi_g$ band system is known to be highly perturbed and high resolution emission studies have revealed the presence of a new nearby $B^2\Delta$ electronic state ^c.

Several hot bands are present on our spectrum. The characterisation of a first band around 30500 cm^{-1} was already revealing the typical structure of a $A^2\Pi_{u3/2} - X^2\Pi_{g3/2}$ band, i. e. strong P and R branches degraded to the red. Molecular parameters have been determined. The analysis is in progress and the results will be reported.

^aY. S. Tang and C. D. W. Wilkinson, *Appl. Phys. Lett.* **58**, 2898 (1991) and ref. therein

^bD. Collet and T. R. Huet, *J. Mol. Spectrosc.*, accepted (1999)

^cJ. C. Choi and J. L. Hardwick, *J. Mol. Spectrosc.* **137**, 138 (1989), **145**, 371 (1991), and ref. therein

UV LASER SPECTROSCOPY USING THE VELOCITY
MODULATION TECHNIQUE : NEW HOT BANDS OF THE
 $B^2\Sigma_u^+ - X^2\Sigma_g^+$ SYSTEM OF N_2^+

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The laser absorption spectroscopy of molecular ions using the velocity modulation technique has been employed in the UV region. The absorption source was a cw single mode laser beam from a cavity frequency doubling unit associated with a dye laser. The high resolution spectrum of the First Negative system $B^2\Sigma_u^+ - X^2\Sigma_g^+$ of N_2^+ has been studied. The N_2^+ ions were produced with an electric discharge in a flowing gas mixture of He/ N_2 . Seven vibrational bands of the $\Delta v=2$ sequence ($v'=2-8$) have been observed in the region between 30000 and 30600 cm^{-1} , and five of them for the first time at high resolution ($v'=2-4,6,7$). A set of seven hundred and seventy lines have been assigned, among them several are extra-lines belonging to the $A^2\Pi_u - X^2\Sigma_g^+$ system. A standard model has been used to consider the perturbations between the rovibrational levels of the $B^2\Sigma_u^+$ and $A^2\Pi_u$ states. An improved set of deperturbed constants and effective interaction parameters were derived for the $v_B=3-v_A=14$ and $v_B=7-v_A=20$ complexes ^a.

^aD. Collet and T. R. Huet, *J. Mol. Spectrosc.*, accepted (1999)

COMPUTATIONAL ANALYSIS OF WATER ABSORPTIONS AT NEAR INFRARED AND VISIBLE WAVELENGTHS

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Water is the major atmospheric absorber in the mid and far infrared regions of the spectrum. In these regions the many strong, pressure broadened water lines lead to blanket absorption of solar radiation across large portions of the spectrum. However the absorption properties of water in the near infrared and visible are much less well understood. In these region absorption by individual water lines is weaker. However the number of weak but significant water absorption can only be guessed at. There is limited laboratory data [1,2] based on experiments performed at Kitt Peak. Recent experiments[3] have extended this data but theoretical analysis is still to be completed. Polyansky et al [4] showed that variational linelists could be used to assign these spectra. One part of this project is therefore the calculation of a new ab initio linelist for water to help assign the various spectra, particularly in the visible and ultraviolet. Such linelists can also be used to generate a total absorption profiles for water. Our linelists are being used to verify statistical procedure that have been suggested by Learner[5] to analyse total absorption based on laboratory measurements. Progress on this project will be reported at the conference.

[1] Camy-Peyret et al. *J. Mol. Spectrosc.*, **113**, 208-228, 1985

[2] Mandin et al., *J. Mol. Spectrosc.*, **116**, 167-190, 1986

[3] Carleer et al., *J. Chem. Phys.*, (in press)

[4] Polyansky et al., *J. Mol. Spectrosc.*, **189**, 291, 1998

[5] Learner, *private communication*, 1998

SUPERSONIC SLIT NOZZLE PLASMAS: AN OVERVIEW

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Transient molecules belong to the chemically most reactive species. This high reactivity, however, also complicates systematic spectroscopic studies, as it is hard to generate large abundances under laboratory controlled conditions. Uniform plasmas with high molecular densities were obtained in electrical discharges in long and cryogenically cooled cells, but the spectroscopy generally suffered from the high rovibrational temperatures and the Doppler limited resolutions. These disadvantages can be overcome by combining supersonic expansions and slit nozzle plasma techniques. The high molecular densities, the relatively long absorption path length, the low rotational temperature and the nearly Doppler free environment make these nozzles ideally suited for high resolution studies on transient species. Our group has focussed on the development of different kinds of such systems. Applications range from cavity ring down spectroscopy and FM-production double modulation spectroscopy on carbon chain radicals in pulsed high pressure plasmas to high resolution direct absorption spectroscopy of ionic complexes in a cw electron impact plasma. The techniques will be discussed.

THE ROTATIONAL SPECTRUM OF IODINE DIOXIDE, OIO

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OIO is an asymmetric prolate rotor ($\kappa = -0.690$) with a 2B_1 electronic ground state. It was formed initially from the products of a microwave discharge in O_2 passing over molecular iodine and later with greater yield in a DC discharge through a mixture of O_2 and I_2 vapor. Although the experiment was hampered by copious solid deposits and apparently inefficient production of OIO, the rotational spectrum was quite prominent in survey scans in the millimeter and submillimeter regions. Facilitated by predictions of fine and hyperfine patterns from ESR results,^a it was eventually possible to identify high J , R branch transitions with $K_c \approx J$. Over 550 ground state transitions and over 160 transitions of the excited bending state have been included in the fits. The transitions cover a wide range of rotational quantum numbers and permit the accurate determination of an extensive set of molecular parameters. The parameters will be compared to those recently published for OBrO^b and OCIO^c and will be interpreted in terms of the molecular geometry, harmonic force field, and electronic structure.

^aJ.R. Byberg, *J. Chem. Phys.* **85**, 4790-4793 (1986).

^bH. S. P. Müller, C. E. Miller and E. A. Cohen, *J. Chem. Phys.* **107**, 8292 (1997).

^cH. S. P. Müller, G. O. Sørensen, M. Birk, and R. R. Friedl, *J. Mol. Spectrosc.*, **186**, 177 (1997).

SPECTROSCOPY OF CHLOROSYL FLUORIDE, FCIO

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FCIO has been proposed as an intermediate in reactions involving ClF, Cl₂O, and ClF₃O, and it has been suggested as a molecule of atmospheric interest. It has been prepared *in situ* by the hydrolysis of ClF₃. Selected transitions of its pure rotational spectrum were searched for in the millimeter and submillimeter regions using predictions based on an analysis of the ν_1 band.^a Low field Stark measurements have been performed in the millimeter region. FCIO is an asymmetric prolate top, $\kappa = -0.8950$ for F³⁵ClO, with a rather small dipole component of 0.093 (4) D along the *a*-axis and a larger one of 1.93 (5) D along the *b*-axis. Transitions with $1 \leq J \leq 66$ and $0 \leq K_a \leq 19$ were observed. Even in the submillimeter region Cl hyperfine splitting was resolved partially. Two low *J* transitions were observed by microwave Fourier transform spectroscopy yielding some information on the ¹⁹F spin-rotation tensor.

Structural parameters, harmonic force constants, and nuclear magnetic shielding parameters were derived and will be compared with data of related molecules, such as ClF₃, ClF, FCIO₂, FCIO₃ and SF₂. High resolution infrared spectra were taken in the regions of the FCl stretching mode and bending mode around 600 and 310 cm⁻¹, respectively. A preliminary analysis indicates that the FCl stretch, at 596.863 cm⁻¹ for F³⁵ClO, is in Coriolis and Fermi resonance with the dark overtone of δ at 617.1 cm⁻¹. A brief progress report will be given.

^aH. S. P. Müller, submitted

ANALYSIS OF THE EMISSION OF THE HS₂ RADICAL FROM
THE \tilde{A}^2A' STATE DETECTED BY NIR FOURIER
TRANSFORM SPECTROSCOPY

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The \tilde{A}^2A' state of the hydrothiosulpheno radical, HS₂, has been observed in emission in a fast flow reactor system. The emission was coupled into a Fourier transform spectrometer and the region between 6400 and 8000 cm⁻¹ recorded. Four rovibrational bands ($1_0^0 2_0^0 3_0^0$, $1_0^0 2_0^0 3_1^1$, $1_0^0 2_1^0 3_0^1$ and $1_0^0 2_0^0 3_1^0$) have been recorded at high resolution. The $1_0^0 2_0^0 3_0^0$ and $1_0^0 2_0^0 3_1^0$ bands have been analysed together with previous microwave data^a to yield high-quality rotational constants for the first electronically excited state.

^aS. Yamamoto and S. Saito, *Can. J. Phys.* **72**, 954 (1994)

**HIGH-RESOLUTION FOURIER TRANSFORM
SPECTROSCOPY OF $^{14}\text{N}_2$ MOLECULE: FIRST
OBSERVATION OF THE $\Delta v = 1$ SEQUENCES OF THE B-W
SYSTEM. GLOBAL ROTATIONAL ANALYSIS OF THE B' $^3\Sigma_u^-$,
W $^3\Delta_u$, B $^3\Pi_g$, AND A $^3\Sigma_u^+$ STATES**

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The extension of high-resolution observation of the electronic emission spectrum of $^{14}\text{N}_2$ toward the infrared domain is presented. To date, rotational analysis of the widely investigated spectrum of the $^{14}\text{N}_2$ molecule have been done in a spectral domain ranging from 2500 cm^{-1} to the UV. We have recorded for the first time the infrared part of the $^{14}\text{N}_2$ spectrum from 1250 to 2500 cm^{-1} , using the Fourier transform spectrometer of Laboratoire de Photophysique Moléculaire (LPPM) at an unapodized resolution of 0.0043 cm^{-1} . Otherwise, spectra covering the 2500 - 17000 cm^{-1} spectral domain have also been recorded allowing us to perform a global rotational analysis of the B' $^3\Sigma_u^-$, W $^3\Delta_u$, B $^3\Pi_g$, and A $^3\Sigma_u^+$ states. Spectroscopic parameters for the first vibrational levels of these states, consistent with those previously reported but with improved accuracy, are obtained from the experimental wavenumbers by a nonlinear least-squares procedure.

DETECTION OF FPO BY HIGH-RESOLUTION INFRARED SPECTROSCOPY

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The short-lived FP=O molecule was first detected by matrix IR spectroscopy¹, and very recently its FT microwave spectrum has been observed². We have produced FP=O in a flow both by reaction of OPFBr₂ with Ag and (more advantageously) by thermolysis of (F₂P)₂O and recorded its mid-IR spectrum with a resolution of ca. $8 \times 10^{-3} \text{ cm}^{-1}$. The a-type ν_1 band (P=O stretch), $\nu_0 = 1297.537\ 24(11)$, was analyzed. Improved ground state constants were obtained by combining ground state combination differences with mw transitions². From a fit of more than 1000 observed transitions, $v_1 = 1$ excited state parameters were determined up to quartic centrifugal distortion constants. Our results are in full agreement with the matrix and the rotational data but disagree with the previously claimed gas phase detection of FP=O by low resolution IR spectroscopy³.

¹R. Ahlrichs, R. Becherer, M. Binnewies, H. Borrmann, M. Lakenbrink, S. Schunck, and H. Schnöckel, *J. Amer. Chem. Soc.* **108**, 7905-7911 (1986).

²B. Gatehouse, T. Brupbacher, and M. C. L. Gerry, *J. Phys. Chem. A* **103**, 560-567 (1999).

³A. M. Allaf and I. Boustani, *Vib. Spectrosc.* **16**, 69-75 (1998).

HIGH-RESOLUTION IR SPECTRUM OF SCF₂ FROM 1000 TO 1400 cm⁻¹: THE $\nu_1/\nu_3 + 2\nu_5/\nu_2 + \nu_3$ AND $\nu_4/\nu_2 + \nu_5$ INTERACTING STATES

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The FT infrared spectrum of SCF₂ has been recorded in the 1000 - 1400 cm⁻¹ region with a resolution of 2.5×10^{-3} cm⁻¹. The rotationally resolved ν_1 and ν_4 band systems have been studied for the first time, and altogether 11500 transitions have been assigned. Both fundamentals are involved in strong anharmonic (Fermi) resonances. Effective centers ($J = K_a = K_c = 0$) of the interacting bands are ν_1 1366.7117 cm⁻¹, $\nu_3 + 2\nu_5$ 1365.4257 cm⁻¹, $\nu_2 + \nu_3$ 1311.1491 cm⁻¹ (a_1 species), and ν_4 1190.0839 cm⁻¹, $\nu_2 + \nu_5$ 1217.8191 cm⁻¹ (b_1 species). The strong K_a - dependence of the $\nu_1 / \nu_3 + 2\nu_5$ level mixing enabled a numerical determination of the interaction constants while the other anharmonic interactions were accounted for by consideration of relative intensities. Deperturbed band centers, anharmonicity constants and excited state rotational and centrifugal distortion constants have been determined. Experimental equilibrium rotational constants were deduced employing previously determined¹ ν_2 , ν_3 , ν_5 and ν_6 parameters.

¹H. Bürger and W. Jerzembeck, *J. Mol. Spectrosc.* **188**, 209-214 (1998).

HIGH-RESOLUTION FTIR SPECTROSCOPY OF VINYL CHLORIDE IN THE REGION OF THE FUNDAMENTAL BANDS ν_{10} AND ν_{11}

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The infrared spectrum of natural $\text{CH}_2=\text{CHCl}$ has been recorded in the range $980\text{--}830\text{ cm}^{-1}$ at a resolution of about 0.005 cm^{-1} by means of a Bruker IFS 120 HR spectrometer. The spectral region investigated is characterized by two strong absorptions: ν_{10} (942.175 cm^{-1}) and ν_{11} (896.572 cm^{-1}), approximately corresponding to the CH_2 wagging and the $\text{C}=\text{C}$ twisting modes, respectively.

$\text{CH}_2=\text{CHCl}$ is a planar molecule belonging to the symmetry point group C_s , and the two examined vibrations are of A'' symmetry, thus giving rise to c -type bands. Since this molecule approaches to a prolate symmetric top ($\kappa \simeq -0.98$) the structure exhibits patterns characteristic of perpendicular bands, mainly in the Q-branch regions that are dominated by a series of almost equally-spaced ${}^P Q_K$ and ${}^R Q_K$ clusters not always displaying a completely resolved J fine structure. The absorptions in the P and R branches show well-resolved details with similar trends in both the fundamentals.

Although the two bands overlap to a great extent producing crowded and irregular absorption patterns, the rovibrational analysis led to an overall assignment of about 5000 transitions of $\text{CH}_2=\text{CH}^{35}\text{Cl}$ with $J \leq 51$, $K_a \leq 12$ for ν_{10} and $J \leq 73$, $K_a \leq 13$ for ν_{11} . Two well-determined sets of upper state constants were obtained by least-squares fits of the identified lines, employing the Watson's A-reduction Hamiltonian in the I' representation. The obtained spectroscopic parameter values, which allow an accurate reproduction of the observed spectra, compare satisfactorily with those of the ground state, thus indicating that the $\nu_{10} = 1$ and $\nu_{11} = 1$ states are essentially free from perturbations.

Details of the investigation are presented and the results of the analysis discussed.

PRECISION FREQUENCY MEASUREMENTS OF NIR SPECTRAL LINES BY DIODE LASER SPECTROMETRY

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We have developed an absorption spectrometer of high sensitivity and measurement precision in the 780-790 nm region by employing two piezo-controlled Fabry-Perot etalons in conjunction with diode laser sources. The first is used to stabilise and frequency track the spectroscopic source, whilst the second calibrating etalon is locked to a spectral line of water or of acetylene in such a manner that its free spectral range becomes precisely known. With this system we have achieved a source stability of 10^{-6} cm^{-1} and a spectral measurement accuracy markedly better than 0.001 cm^{-1} . Sample spectra for both of the above species are presented, and a comparison is made between our results and those of Flaud et al (1) and the HITRAN database in this region.

(1) J.-M. Flaud, C. Camy-Peyret, A. Bykov, O. Naumenko, T. Petrova, A. Scherbakov and L. Sinitza, *J. Mol. Spectrosc.* **183**:2 (1997) 300.

**HIGH RESOLUTION DIODE LASER SPECTROSCOPY OF
THE NIR BANDS OF PROPYNE IN THE
12730 – 12790 cm⁻¹ RANGE**

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The $3\nu_1 + \nu_3 + \nu_5$ band and $3\nu_1 + \nu_3 + \nu_5 + \nu_{10} - \nu_{10}$ band of propyne together form a dense and overlapping spectral structure in the 12730 cm⁻¹ to 12790 cm⁻¹ range. By using high resolution diode laser spectroscopy, we have been able to measure and analyse this structure in sufficiently fine detail to derive a large number of excited state rotational and centrifugal distortion parameters for these two states. Current best estimates (all in cm⁻¹) are:

	$3\nu_1 + \nu_3 + \nu_5$	$3\nu_1 + \nu_3 + \nu_5 + \nu_{10}$
<i>A</i>	5.30020(12)	5.29987(28)
<i>B</i>	0.280569(7)	0.2814626(64)
<i>D^J</i>	$4.8(5) \times 10^{-8}$	$6.47(36) \times 10^{-8}$
<i>D^{JK}</i>	$6.04(8) \times 10^{-6}$	$2.43(53) \times 10^{-6}$
<i>D^K</i>	$7.62(12) \times 10^{-5}$	$-1.37(72) \times 10^{-5}$
<i>q₁₀</i>	$-1.807(85) \times 10^{-4}$	

These data show marked discrepancies from those given in previously published work (1), and envelope simulations corresponding both to our results and to the latter are compared with our experimental spectra.

(1) Z. Lin, K. Boraas and J.P. Reilly, *J. Mol. Spectrosc.* **156** (1992) 147

THE HIGH RESOLUTION FAR-INFRARED SPECTRUM OF VINYLAMINE

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The molecular structure and potential of vinylamine has been the subject of several spectroscopic and theoretical studies. Despite this large amount of work, the vibrational spectrum of vinylamine is not well understood and not uniquely assigned due to complexities arising because of the inversion motion. Two different assignments are well argued in the literature [1,2,3]. The present work has been carried out in an attempt to clarify the vibrational assignment and to further understand the molecular potential of the molecule.

The infrared spectrum of vinylamine, generated by pyrolysis of cyclobutylamine has been investigated at low and high resolution. The ro-vibrational structure of the far infrared spectrum (0.002 cm^{-1}) has been analysed and effective rotational and centrifugal distortion constants derived for eight vibration-rotation bands in the region $250\text{-}750\text{ cm}^{-1}$. The ro-vibrational structure of two further bands has been assigned using combination differences and some conclusions drawn about the vibrational energy levels involved. With the large amount of new data it is possible to clear up some misassignments and achieve a vibrational analysis of the far infrared region, but not to totally exclude an alternative assignment.

Further progress on an understanding of the spectrum and potential function of vinylamine is dependent on the development of a more appropriate model that can handle two or more coupled large amplitude motions,

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- (1) Y. Hamada, N. Sato and M. Tsuboi, *J. Mol. Spectrosc.* 124, 172-178 (1987)
 - (2) R. D. Brown, P. D. Godfrey, B. Kleibomer, A. Pierlot and D. McNaughton, *J. Mol. Spectrosc.* 142, 195-204 (1990)
 - (3) D. McNaughton and E. G. Robertson, *J. Mol. Spectrosc.* 163, 80-85 (1994)

THE PERPENDICULAR FUNDAMENTAL ν_5 OF
CHLOROFORM $^{12}\text{CH}^{35}\text{Cl}_3$: HIGH RESOLUTION INFRARED
STUDY OF THE ν_5 BAND TOGETHER WITH THE
MILLIMETER-WAVE ROTATIONAL SPECTRUM

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The infrared spectrum of the perpendicular fundamental ν_5 of chloroform around 776 cm^{-1} has been studied with two high resolution methods. A short range from the central part of the spectrum was measured with a diode laser by using a cold jet sample including natural chloroform. More than 100 rotational lines of $^{12}\text{CH}^{35}\text{Cl}_3$ could be assigned. The whole band region was measured with a Fourier transform spectrometer at a resolution of 0.0010 cm^{-1} and by using an isotopically pure $\text{CH}^{35}\text{Cl}_3$ sample. Starting from the results of the diode laser investigation more than 2000 lines could be assigned with $J_{max} = 91$ and $K_{max} = 58$. In addition to the infrared spectra also millimeter-wave lines were measured. Altogether 58 lines corresponding to J values 22, 23 and 35 at the excited vibration state $\nu_5 = 1$ were assigned and analysed. All the data from three different spectra were simultaneously fitted and e.g. the results $\nu_0 = 775.96150(3)\text{ cm}^{-1}$, $B_5 - B_0 = -0.180171(22) \times 10^{-3}\text{ cm}^{-1}$, $C_5 - C_0 = -0.17057(15) \times 10^{-3}\text{ cm}^{-1}$, and $(C_z)_5 = 0.0475294(11)\text{ cm}^{-1}$ were obtained.

ABSOLUTE LINE INTENSITIES AND BROADENINGS FOR THE 3-0 BAND OF $^{12}\text{C}^{16}\text{O}$

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Absolute line intensities, vibrational transition moment, Herman-Wallis factor and self-broadening coefficients for the 3-0 vibration-rotation band of $^{12}\text{C}^{16}\text{O}$ are determined^a from absorption Fourier transform spectra with about $6 \times 10^{-3} \text{ cm}^{-1}$ unapodized resolution. The range of the CO measurements extends from P(20) at 6254 cm^{-1} to R(20) at 6407 cm^{-1} . The fitted squared transition dipole moment $|\mu_0^3|^2$ and Herman-Wallis factor coefficients C and D are respectively equal to $(1.6727 \pm 0.0014) \times 10^{-7} \text{ Debye}^2$, and $(1.204 \pm 0.005) \times 10^{-2}$ and $(1.08 \pm 0.05) \times 10^{-4}$ when given with one standard deviation. The absolute value of $|\mu_0^3|^2$ is equal to $(1.67 \pm 0.1) \times 10^{-7} \text{ Debye}^2$. The present results agree well with those published on the intensities, years ago, by Toth et al.^b, and Bouanich et al.^c. The recent work by Henningsen et al.^d reports line strengths and self-broadening parameters determined on the 3-0 band of CO from the measurement of 21 lines in the R-branch with a diode laser. The comparison between their line intensities and ours shows no overall discrepancies, but a J-dependent diverging deviation. Their transition moment is given equal to $(4.10 \pm 0.02) \times 10^{-4} \text{ Debye}$ (squared value : $(1.68 \pm 0.17) \times 10^{-7} \text{ Debye}^2$). This is consistent with our value. Their broadening coefficients agree with ours as well. The latest version of HITRAN database^e reports line intensities calculated from the dipole moment function of Chackerian and Tipping^f. These intensities are greater than ours by about 7 % with no J-

^aN. Picqué, G. Guelachvili, V. Dana, J.-Y. Mandin, *J. Mol. Struct.*, special issue honoring G. Graner, in press, 1999.

^bR. A. Toth, R. H. Hunt, E. K. Plyler, *J. Mol. Spectrosc.* **32** (1969) 85.

^cJ. P. Bouanich, Nguyen-Van-Thanh, I. Rossi, *J. Quant. Spectrosc. Radiat. Transfer*, **30** (1983) 9.

^dJ. Henningsen, H. Simonsen, T. Møgelberg, E. Trudsø, *J. Mol. Spectrosc.* **193** (1999) 354.

^eL. S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.-M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, and P. Varanasi, *J. Quant. Spectrosc. Radiat. Transfer*, **60** (1998) 665.

^fC. Chackerian Jr, and R.H. Tipping, *J. Mol. Spectrosc.*, **99** (1983) 431.

dependence. The line intensities measured by Fukasori et al.^g, and Chackerian et al.^h, where no individual line information is given, are also said to be 5-10 % smaller than HITRAN96. The line-broadening parameters are also reported to be presently under study by Hnatovsky et al.ⁱ.

^gM. Fukasori, T. A. Aoki, T.E. Aoki, H. Ishida, T. Watanabe, HITRAN Database Conference, 23-25 Sept. 1998, p 6, Hanscom AFB, MA.

^hC. Chackerian Jr, R.J. Kshirsagar, L.P. Giver, L.R. Brown, Fourier Transform Spectroscopy: New Methods and Applications, 22-24 June 1999, Santa Barbara, CA.

ⁱC. Hnatovsky, A. Predoi-Cross, K. Strong, J.R. Drummond, Fourier Transform Spectroscopy: New Methods and Applications, 22-24 June 1999, Santa Barbara, CA.

HCN/HNC BETWEEN 2 AND 5 μm : FOURIER TRANSFORM EMISSION SPECTRA OF ASTROPHYSICAL INTEREST

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HCN is a well-known important interstellar molecule. Through its numerous overtone, combination and hot bands, it makes a large contribution to the opacity of carbon stars. Especially, the recent ISO (Infrared Space Observatory) spectra reveal^a a forest of emission lines, from the well-known CO and from vibrationally excited HCN, which have to be modelled to detect other species of interest. The HCN vibrational and rotational temperatures in these media are reported to be around 700-1500 K in the carbon-rich circumstellar envelope of IRC+10216.

An important amount of work has already been accomplished on HCN in the infrared. Up to 1994, it is compiled in Ref.^b. Recently, exhaustive studies on line positions^c between 500 and 10 000 cm^{-1} and on intensity measurements of fundamental^d, hot bands^e and other weak transitions^f have been reported from absorption Fourier transform (FT) spectra by Maki and coworkers. Preliminary results of emission spectra of the bending modes of HCN in a heated cell have also been presented^g by the Giessen group.

In the present work^h, a FT emission spectrum from a radio-frequency excited plasma between 2400 and 3400 cm^{-1} is reported. This region corresponds in particular to the near infrared spectral range, observed thanks to the ISO Short Wavelength Spectrometer. These measurements should provide

^aJ. Cernicharo et al., *Astron. Astrophys.* **315** (1996) L201.

^bG. Guelachvili, and K.N. Rao, *Molecular Constants mostly from Infrared Spectroscopy. Linear Triatomic Molecules.*, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, G. Guelachvili Ed., Springer Verlag Volume II/20, Subvolume B1 pp. 1-474 (1995)

^cA. Maki, W. Quapp, S. Klee, G.C. Mellau and S. Albert, *J. Mol. Spectrosc.* **180** (1996) 323.

^dA. Maki, W. Quapp, S. Klee, G.C. Mellau and S. Albert, *J. Mol. Spectrosc.* **174** (1995) 365.

^eA. Maki, W. Quapp, and S. Klee, *J. Mol. Spectrosc.* **171** (1995) 420.

^fA. Maki, W. Quapp, S. Klee, G.C. Mellau and S. Albert, *J. Mol. Spectrosc.* **185** (1997) 356.

^gG. Ch. Mellau, M. Winnewisser, and B.P. Winnewisser, Poster J21, 15th International Conference on High Resolution Spectroscopy, Prague (Czech Republic), 30.8-3.9.1998.

^hN. Picqué, G. Guelachvili, *Spectrochimica Acta A*, 1999 (in press).

a complementary dataset to the existing ones, which are only obtained from absorption experiments. They are performed under experimental conditions, thermodynamically closer than the laboratory absorption spectra, to the HCN formation conditions in the circumstellar envelopes. The molecular constants, for 21 vibration-rotation bands are given, as well as estimates of first-order Herman-Wallis coefficients for 11 bands. These constants are derived from about 900 $\text{H}^{12}\text{C}^{14}\text{N}$ observed transitions, and are used to generate a sequential linelist of about 1400 calculated line positions, within a standard deviation equal to $3 \cdot 10^{-4} \text{ cm}^{-1}$. The ν_1 band of $\text{H}^{14}\text{N}^{12}\text{C}$ is simultaneously observed with a weak signal-to-noise ratio, and its relative line intensities are given.

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LINESHAPE STUDY OF MILLIMETER TRANSITIONS OF CO AND O₃ PERTURBED BY N₂ AND O₂

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We report on collisional relaxation effects on the J=3-2 line of CO and on the J =3_{4,32}-3_{4,33} line of O₃ perturbed by nitrogen and oxygen. Measurements have been made by using a video-type spectrometer at different temperatures in the 240-400 K range. In the pressure range investigated (20-400 mTorr of perturber gas) observed line profiles give a strong evidence of departures from the usual Voigt profile. These features are characteristic of line narrowing effects which may result from molecular diffusion (Dicke effect) and speed dependent relaxation rates.

The CO line has been first studied in details. In this purpose, a quasi analytical Speed Dependent Galatry Profile is proposed, which allows perfect fits of observed signals. However a perfect linear correlation between the parameters describing the molecular diffusion and the speed dependence of relaxation rates is observed. Calculations using the Robert-Bonamy collisional theory and the Brownian motion one allow to discuss this correlation.

This analysis has been extended to our O₃ line results. The same features are observed and a similar linear correlation is observed between narrowing parameters.

Finally retrieved relaxation parameters and their temperature dependences are compared to previous reported measurements.

LINE INTENSITIES AND PRESSURE BROADENING OF ALL OZONE FUNDAMENTALS

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Although numerous spectroscopic investigations of ozone have been conducted in the past, the accuracy of line intensity (desired 1%) and air broadening (desired 5%) is not satisfactory for atmospheric remote sensing and climate modelling applications. New measurements have been performed covering all fundamentals simultaneously applying a coolable 25 cm absorption cell with a Bruker IFS 120 HR. Measurements of pure ozone in the range from 0.2 to 9 hPa as well as pressure broadened measurements with nitrogen and oxygen up to 50 hPa within a temperature range of 190 to 300 K were performed. The retrieval of line parameters from the numerous spectra containing thousands of lines required sophisticated automatised software. Transition moment expansion coefficients together with centrifugal distortion constants were fitted and will be presented. Line broadening parameters have been expressed as polynomials in the total angular momentum quantum number within a particular subband. Quality assurance of the methods is given by validated intensity measurements in the FIR^a and validated pressure broadening measurements by comparison of two independent methods^b.

^aM. Birk, G. Wagner and J.-M. Flaud, "Experimental Linestrengths of Far-Infrared Pure Rotational Transitions of Ozone"; *J. Molec. Spectrosc.*, 163, 245-261 (1994)

^bFinal Report of "Study on a Spectroscopic Database for Millimeter and Submillimeter Wavelengths", ESTEC/Contract No 11581/95/NL/CN

**SPEED-DEPENDENT BROADENING AND LINE MIXING IN
CH₄ PERTURBED BY AR AND N₂ FROM
MULTISPECTRUM FITS**

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Speed-dependent broadenings and shifts have been determined for the P and R branches of the ν_3 band of CH₄ perturbed by Ar and N₂ using a multi-spectrum fitting analysis of high-resolution tunable difference-frequency laser spectra recorded at pressures ≤ 67 kPa. For $J \geq 3$, the tetrahedral fine structure components in each J manifold are collisionally coupled and exhibit significant interference. The coupled lines are treated using a speed-dependent first-order line mixing profile and are compared to a speed-independent full relaxation matrix inversion procedure with off-diagonal coupling elements calculated from an atom-atom Lennard-Jones potential model.

POSITIONS AND INTENSITIES OF AMMONIA HOT BANDS IN THE 5 TO 8 μm REGION AND IN THE 4 μm REGION

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To complete our infrared analyses of $^{14}\text{NH}_3$ between 5 and 8 μm , a region dominated by the absorption of the $2\nu_2$ overtone and ν_4 fundamental bands, we have also modeled the $3\nu_2 - \nu_2$ and $\nu_2 + \nu_4 - \nu_2$ hot band line positions and intensities measured at 0.005 cm^{-1} resolution with the Fourier transform spectrometer located at the Kitt Peak National Observatory. Using the $3\nu_2$ and $\nu_2 + \nu_4$ upper states energy obtained previously, ^a several hundred line positions with J up to 10 have been assigned to $3\nu_2$ (s) - ν_2 (a), $3\nu_2$ (a) - ν_2 (s), $\nu_2 + \nu_4$ (s) - ν_2 (s) and $\nu_2 + \nu_4$ (a) - ν_2 (a) located around 1416, 1963, 1608 and 1618 cm^{-1} respectively. Selected intensity measurements have been modeled as well. In the 4 μm region which is dominated by the absorption of the $3\nu_2$ overtone and the $\nu_2 + \nu_4$ band, we have found a number of lines belonging to the hot bands $\nu_1 - \nu_2$, $\nu_3 - \nu_2$ and $2\nu_4 - \nu_2$ using the upper state parameters determined in our previous study in the 3 μm region. ^b We have confirmed assignments involving the $4\nu_2$ (s) overtone centered around 3462 cm^{-1} by identifying $4\nu_2 - \nu_2$ transitions. This work provides a first analysis of ammonia hot bands near the 5 μm window being used to monitor atmospheres of planets and cool stars. ^c

^aI. Kleiner, G. Tarrago, and L. R. Brown, *J. Mol. Spectrosc.* **173**, 120-145 (1995).

^bI. Kleiner, L. R. Brown, G. Tarrago, Q-L. Kou, N. Picque, G. Guelachvili, V. Dana and J-Y. Mandin, *J. Mol. Spectrosc.* **193**, 46-71 (1999).

^cPart 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.

A NEW MULTIPLIER TERAHERTZ SPECTROMETER

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Presently the Cologne THz Spectrometer covers the region from 50 GHz to 1.2 THz using Backward Wave Oscillators (BWOs) as direct frequency sources. Frequencies higher than 1.8 THz are measured with the Cologne Sideband Spectrometer. In order to close the frequency gap between both spectrometer we are currently setting up a new spectrometer based on frequency multiplication. The multiplier^a generates harmonics of a fundamental frequency, which is produced by a BWO. Key elements are a planar Schottky diode and an output backshort. With these it is possible to tune the cavity to the desired output frequency with sufficient power at higher frequencies. First measurements with the multiplier will be shown. The high efficiency of the multiplier is demonstrated by measuring the CO $J = 12 \leftarrow 11$ transition at 1382 GHz using the sixth harmonic of the BWO fundamental mode. High resolution spectra of HCN in the range of 265-1600 GHz with an accuracy of 1 KHz and improved molecular parameters will additionally be presented.

^aF. Maiwald, F. Lewen, B. Vowinkel, W. Jabs, D.G. Paveljev, M. Winnewisser, G. Winnewisser, *IEEE Microwave and Guided Wave Letters*, **9**, (1999), in press

HIGH RESOLUTION ANALYSIS OF THE $A^2\Pi-X^2\Sigma^+$ SYSTEM OF *MgCl*

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The $A^2\Pi-X^2\Sigma^+$ emission system of the *MgCl* molecule has been reinvestigated by means of Fourier Transform Spectroscopy (FTS). The *MgCl* species were produced by mixing Mg vapour with a gaseous flow of a He/Cl₂ and excited in a heated Schüller's type discharge tube. Rotational analysis of the sub-bands 0-0, 1-1 and 0-1 has been performed improving the molecular constants previously reported^b.

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^bM. Singh, G. S. Ghodgaokar and M. D. Saksena, *Can. J. Phys.*, **65**, 1594-1603 (1987)

QUANTUM DYNAMICS OF BENDING VIBRATIONS OF THE CH CHROMOPHORE IN SYMMETRIC AND ASYMMETRIC METHANE ISOTOPOMERS

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The time dependent quantum dynamics of the alkyl CH chromophore is investigated by calculation of the wave packet evolution after coherent excitation of the bending modes within the methane isotopomers CHD₃, CHD₂T and CHDT₂ using realistic potential energy surfaces and electric dipole moment functions^b. Results include discussions on different excitation pathways depending on the bending direction in an internal coordinate frame, the role of quasiclassical and delocalized intramolecular vibrational redistribution on these processes^c and a possibility of controlling the dynamics by localization of the wave packet motion in subspaces of the relevant configuration space. Bending excitation is also used to generate dynamical chirality^d. The subsequent free evolution of the wave packet after generation of a chiral molecular structure corresponds to a stereomutation reaction on the femtosecond time scale superimposed by a racemization process, which is understood as arising from coherent delocalization effects of intramolecular vibrational redistribution. Possibilities of controlling the time evolution of chirality are discussed in a semi-quantitative way by calculation of the time dependent enantiomeric excess.

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MODE SELECTIVE STEREOMUTATION IN HYDROGEN
PEROXIDE: 6D TUNNELLING AND WAVE
PACKET DYNAMICS

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As the first in the series of the dihydrogendichalcogenides H_2X_2 and related compounds, which show chirality by C_2 symmetry in their equilibrium geometry, H_2O_2 is among the simplest prototypes for stereomutation, albeit in the low barrier limit.^{a,b} This reaction can be considered as one of the most fundamental isomerisations in chemistry. The full quantum dynamics for this particularly simple transformation from the left handed into the right handed enantiomer of hydrogen peroxide isotopomers is studied both from the point of view of the spectroscopic states and using explicitly time dependent wavepacket dynamics. The six dimensional tunnelling dynamics of H_2O_2 , HOOD, and D_2O_2 are investigated on a recently developed analytical global potential energy hypersurface for the electronic ground state of hydrogen peroxide.^c A new formulation of the harmonic reaction path hamiltonian approximation^d gives good agreement with the results of a new fully coupled six dimensional adiabatic channel approach.^e The experimentally observed pure torsional spectrum and mode specific tunnelling are well reproduced, as are the few known isotope shifts. 6D time dependent wavepacket dynamics confirm the adiabaticity of the stereomutation. Predictions are made for the torsional tunnelling spectrum of HOOD and D_2O_2 as well as for the stereomutation dynamics of H_2O_2 at very high excitations.

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MICROSOLVATION OF FUNDAMENTAL CARBOCATIONS

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Infrared photodissociation spectra of mass selected $\text{CH}_3^+ \text{-Rg}_n$ and $\text{C}_2\text{H}_2^+ \text{-Rg}_n$ complexes ($\text{Rg} = \text{He, Ne, Ar, } n = 1\text{-}8$) have been recorded in the spectral range of the CH stretch fundamentals and their first overtones. The spectra of dimers and trimers display rotational resolution and provide detailed information about the intermolecular potential energy surfaces and the bonding mechanisms. In the case of larger clusters, the analysis of vibrational frequency shifts and photofragmentation branching ratios allows for the development of a detailed picture of the cluster growth process. The experimental results are in good agreement with ab initio calculations at the MP2 level.

**JET-FTIR SPECTROSCOPY OF MEDIUM STRENGTH
HYDROGEN BONDING COMPLEXES OF B:H(D)X
(B=DIMETHYLETHER, X=CL, F)**

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FTIR spectra of the ν_s bands of H(D)Cl and H(D)F complexed by dimethylether in a supersonic jet expansion seeded with argon have been recorded using a new experimental set-up which improves our previous data [1]. The temperature effects introduced in the experiments coupled to jet-cooled conditions (<50 K) facilitate the band assignments and enable some parameters relative to these complexes to be estimated with the support of Density Functional calculations. From this analysis a new interpretation of the band shaping mechanisms for the gas cell spectra of DME:H(D)Cl and DME:H(D)F dimers, which emphasizes the role played by the transitions involving the low frequency intermolecular bending modes ν_δ , is proposed.

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COULOMB EXPLOSION IMAGING AND THE CH₂⁺ MOLECULE

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It has been conjectured, on the basis of the interpretation of data obtained using the Coulomb explosion imaging (CEI) method,^a that there is a large nonadiabatic contribution to the wavefunctions of low-lying CH₂⁺ states, beyond that coming from the Renner effect. We have calculated *ab initio* the energies of the lowest excited electronic states and find, in agreement with results already in the literature,^b that the excited electronic states of CH₂⁺ are at much too high an energy (greater than 6 eV) for such nonadiabatic interaction to be significant. To compare with the CEI results we calculate the Boltzmann averaged bending angle distribution using our previously calculated *ab initio* potential energy curves of the \tilde{X} , \tilde{A} pair of Renner interacting potentials,^c and make full allowance for the Renner effect in the calculation of the wavefunctions. This *ab initio* calculation leads to a distribution that is significant over a narrower range of bending angles than that obtained experimentally by the CEI method. Depending on the accuracy of the CEI distribution this could indicate an error in the *ab initio* potential energy surfaces. We have modified the shape of the \tilde{X} -state surface in order to approximately reproduce the CEI result, and the change we have to make is rather large. An experimental determination of some of the bending energy level separations for CH₂⁺ would be a more definitive way of testing the shape of the potential surface.

^aA. BAER, M. GRIESER, L. KNOLL, J. LEVIN, R. REPNOW, D. SCHWALM, Z. VAGER, R. WESTER, A. WOLF, AND D. ZAJFMAN, *Phys. Rev. A* **59**, 1865 (1999).

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ELECTRONIC STRUCTURE INCLUDING SPIN-ORBIT EFFECTS FOR THE DIMERS OF RUBIDIUM AND CESIUM

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Being involved for some years in predictions of molecular states of homonuclear alkali dimers in their long-range part through specific models we proposed, we were incited to extend our investigations by predicting potential energy curves in the whole range of internuclear distance R . In this aim we performed calculations using the packages CIPSI and CIPSO of the 'Laboratoire de Physique quantique de Toulouse, France'. Briefly sated the method used is as follows. The alkali atoms Rb and Cs are described via non-empirical one-electron pseudopotentials and Gaussian basis sets, l -dependent core polarisation potentials are included to take into account core-valence effects and a full valence Configuration Interaction calculation CI is performed for molecular states in Hund's case a. Spin-orbit effects are taken into account via semi-empirical spin-orbit pseudopotentials we derived for Rb and for Cs. The adiabatic states in Hund's case c are provided by diagonalizing the total hamiltonian including spin-orbit pseudopotentials in the molecular basis of case a. Results will be presented for all the molecular states dissociating up to $5s+7s$ for the dimer of rubidium and up to $6p+6p$ for the dimer of cesium. Comparison with photoassociative spectroscopy data and with long-range predictions will be discussed.

AN IMPROVED POTENTIAL ENERGY CURVE FOR THE GROUND STATE OF NaK

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In view of the renewed interest in the long-range interactions between alkali atoms which has arisen with the developments of photoassociation techniques in ultracold alkali species, we have recorded A-X emission from the NaK molecule, observing vibrational levels up to $v = 70$ in the ground state. A cw tunable dye laser (LD 700 dye) was used to excite selected levels of the $A\ ^1\Sigma_u^+$ state, supplying a balanced spread of observations in v'' and J'' of the $X\ ^1\Sigma_g^+$ state, particularly for the high-lying vibrational levels of the ground state.

A potential curve has been constructed up to $v = 68$ using the IPA method^a. This curve extends to $10.6\ \text{Å}$. An asymptotic method has been used to extrapolate to the dissociation limit, fitting all available data with above $v \geq 63$ to determine the dissociation energy, Coulombic parameters C_6 , C_8 and asymptotic exchange parameters. The dissociation energy obtained is $D_e = 5273.6 \pm 0.2\ \text{cm}^{-1}$, and the coefficient for the leading dispersion term is $C_6 = 2390 \pm 130\ \text{a.u.}$

Near-dissociation expansions provide another route to the dissociation energy. Fitting the vibrational energies for all observed v to a series of expressions of the form :

$$G_v = D_e - X_0 (n=6, C_6, \mu) \cdot (v_D - v)^3 [L/N]$$

where L and N are polynomials in $(v_D - v)$, we find $v_D = 74.1 \pm 0.2$ and confirm our value of D_e .

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A NEW PREDISSOCIATION OF N_2^+ REVEALED BY FAST ION BEAM LASER SPECTROSCOPY AND ATTRIBUTED TO THE $A^2\Pi_u$ STATE

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The molecular nitrogen N_2^+ plays an important role in various atmospheric phenomena as well as in plasmas and discharges containing nitrogen. They are a lot of experimental and theoretical works on the spectroscopy of this interesting molecular ion ^a. From the birth of the laser spectroscopy, new results were obtained for the two well-known electronic transitions $B - X$ and $A - X$, the last one also named Meinel transition ^b. N_2^+ is well appropriate to the fast ion beam laser spectroscopy. The $B - X$ transition has been the subject of very high resolution works where the HFS was resolved ^c and where the predissociation of the B state was observed ^d. In this work, we present the results obtained by fast ion beam laser spectroscopy on the Meinel transition $A - X$ in the visible domain, around 17500 cm^{-1} . Because with a beam, we are in a collisionless situation, the molecular ions remain populated in very high vibrational levels of the ground state. So starting from $v''=33$, it is possible with a visible laser radiation to probe vibrational levels of the A electronic state near the dissociation limit ($v'=60, 61, 62$). These levels show a weak predissociation in the rotational lines with a dissociative lifetime of about 300 picoseconds.

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COHERENT CONTROL OF ROTATIONAL WAVE PACKETS IN LINEAR MOLECULES

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Rotational energy levels in CO₂ are excited using a sequence of two identical, temporally separated 80 fs laser pulses created using an optical Mach-Zehnder interferometer. Each polarized pulse has a sufficiently large bandwidth in order to produce the formation of rotational superposition states – rotational coherence – in the lower electronic state of the molecule. At time zero, a first pump pulse excites spatially aligned molecules which then dephase as a consequence of the rotational motion. At latter time, transient realignment of the molecules occurs whose recurrences give information about the molecular structure. These rotational quantum beats, produced by orientational anisotropy in the sample, are observed by monitoring the polarization of a probe pulse versus time. At time τ , a second pump further excites the molecules at a specific phase of the rotational coherent states evolution producing therefore quantum interference in the overall signal. Temporal interferograms (signal versus τ) are recorded between 0 and 50 ps delay time. At long time ($\tau >$ pulse duration) the signal results in a low frequency periodic oscillation produced by the beatings between the different interfering rotational frequencies. Close to zero delay, the interferogram is dominated by the optical interference producing a modulation of the signal at the laser frequency. The discrete Fourier transform of the temporal interferogram gives the spectrum of the rotationally excited levels.

MANIFESTATION OF THE STRONG QUADRUPLE LIGHT MOLECULE INTERACTION IN THE SURFACE ENHANCED OPTICAL EFFECTS

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As it is well known there is a series of optical effects, arising on molecules, adsorbed on rough surfaces, having significantly larger cross-sections, than the molecules situated in a free space. They are SERS, enhancement of infrared absorption, SEHRS, enhancement of luminescence and some others. For a long time the nature of these phenomena was not clear in full. However in [1,2] it was demonstrated, that the reason of SERS and the enhancement of infrared absorption is quadruple light-molecule interaction, arising in surface fields, strongly varying in space near rough surfaces. These fields are strongly heterogeneous in space and in fact refer to random fields. At present the theory explains why the surface enhanced processes arise on rough surfaces, island films, tunnel junctions and other objects. It explains the nature of so-called active sites, the short range enhancement or the first layer effect, the long range enhancement and its height dependence, the absence of polarization dependence for arbitrary rough surfaces, the frequency dependence of SERS and some other phenomena. Of special importance is possibility of explanation of regularities of the enhanced spectra. It was demonstrated theoretically, that for symmetrical molecules the most enhanced bands are caused by totally symmetric vibrations and by the vibrations, transforming as the d_z component of the dipole moment, which is perpendicular to the surface. Besides the most enhanced band among this group is the band caused by the breathing mode. Depending on the symmetry group of the molecule there may appear lines, which are forbidden in the usual Raman scattering. For molecules, belonging to the symmetry group, where the d_z moment transforms not after the unitary irreducible representation there will be strong lines forbidden in the usual Raman scattering, caused by the scattering via this moment. For the enhancement of infrared absorption peculiarities of the enhanced spectra are similar. The most enhanced bands are caused by the totally symmetric vibrations and by those transforming as the d_z moment. Besides the most enhanced band must be the one caused by the breathing mode. These regularities are well observed experimentally on a large number of symmetrical molecules. Recently it appears, that the SERS system with special conditions can enhance the SERS cross section of separate lines in the range 10 in the 10th - 10 in the 15th power. Those enormous enhancement usually realizes in

colloidal solutions of silver or gold particles and small number of investigated molecules. In the works of Kneipp et al there was the relation 0.6 molecule per particle. This result create a base for the single molecule spectroscopy by SERS method. As it appears from estimations with the quadruple theory of SERS the results of Kneipp can be corroborated. Moreover, in accordance with the work [4] the most active particles have faceted or rod-like form. The last result is in the frameworks of the quadruple SERS theory created in the past [5]. Thus the sensitivity of the SERS method may be made very high and now we have a good base for development of this highly sensitive method.

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VIBRATIONAL SPECTRA OF C_6H_6 , C_6D_6 AND OF C_6D_5H

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The anharmonic force field of C_6H_6 has been calculated with the density functional B3LYP using a TZ2P atomic basis set, by means of a finite difference method. The calculated anharmonic constants x_{ij} , g_{ij} , and r_{ij} , combined with fundamentals were used to assign parallel bands observed in the Raman spectra of benzene, taking into account also Fermi resonances.

The spectra were recorded in Florence at LENS laboratory from 450 to 3200 cm^{-1} at a resolution of 0.7 cm^{-1} , using a multipass cell, an Ar laser ($\lambda = 514nm$, 800 mW of power) and a CCD detector.

The hot bands structure accompanying the ν_1 , ν_2 , $2\nu_4$, $2\nu_{14}$ and $2\nu_{16}$ parallel bands has been analysed and the anharmonic differences between the hot bands origins and the corresponding cold band origin are compared to the theoretical ones. The vibrational level have been calculated taking into account anharmonicity, l-vibrational doubling and Fermi interactions within 100 cm^{-1} . The Raman spectra of C_6D_6 recorded at LENS from 600 to 2500 cm^{-1} at 0.7 cm^{-1} of resolution are being analysed as well, using the results of the anharmonic force field calculations made by Maslen et al.^a. The first results of the analysis will be shown.

The results of calculations made on benzene were extended to C_6D_5H and the list of harmonic fundamentals obtained. Some IR active bands of this molecule were observed in the IR spectra of $^{12}C_6D_6$ and the list of experimental fundamentals is implemented with more accurate wavenumbers of the ν_4 , ν_5 , ν_{10b} , ν_{11} modes of B_1 symmetry observed at 612.6, 922.9, 708.92 and 512.06 cm^{-1} , respectively, and of the ν_{9b} mode at 986.45 cm^{-1} , of B_2 symmetry, (the numbering is according to the scheme of Wilson).

The hot bands structure of the ν_5 and ν_{10b} has been analysed using the anharmonic constants calculated by Maslen et al.^a.

^aP.E. Maslen, N.C. Handy, R.D. Amos and D. Jayatilaka, *J. Chem. Phys.* **97**,4233 (1992).

INFIA - PROGRAM FOR ROTATIONAL ANALYSIS OF LINEAR MOLECULE SPECTRA

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A software package for spectrum rotational analysis is described. The Infia program features multiple simultaneous views to the analysis data, including a spectrum view with assignment markers, a Loomis-Wood type view and lists of assignments, bands and vibrational states. Automatic combination difference prediction and parameter calculation are included for linear molecules, but the program can be also used to assign spectra for symmetric top molecules. The interactive nature of the program combined with high level of automatization makes possible rapid and reliable analysis even for difficult spectra with many overlapping bands and high density of peaks.

Invited Lectures I

Wednesday, September 8, 9:00

Chairman : P. R. BUNKER

**THE PAST, PRESENT AND FUTURE
OF QUANTUM CHEMISTRY**

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EDWARD F. VALEEV, ROLLIN A. KING, MATTHEW L.
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Quantum chemistry, the application of quantum mechanics to molecular problems, has evolved into an indispensable tool for guiding and interpreting experimental chemical physics. The most important contributions to this evolution over the last thirty years will be discussed, including the development of the GAUSSIAN programs, coupled cluster theory, and density functional theory. In addition, the most fertile areas of research for the beginning of the next millennium are considered, including extension of standard methods to molecules of biological interest, high accuracy techniques, and reaction dynamics.

**AB INITIO STUDIES ON VIBRATION-ROTATION SPECTRA
OF REACTIVE MOLECULES**

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High-level ab initio methods can provide accurate potential energy surfaces which contain much spectroscopically useful information. One possible approach to extract such information involves the ab initio computation of harmonic and anharmonic force fields followed by a rovibrational perturbation treatment to yield the familiar spectroscopic parameters. The lecture will first review the current status of this approach, in particular with regard to the convergence of the theoretical results with respect to improved correlation treatments and basis set extension. In collaboration with experimental groups, we have applied this approach to study a number of small reactive species, including difluorovinylidene, silaethene, and difluorosilanethione, where the ab initio predictions have guided the spectroscopic identification of these molecules and facilitated the analysis of their high-resolution spectra. Some examples of these joint investigations will be discussed. The final part of the lecture will address the usefulness and the limitations of density functional theory in studying vibration-rotation spectra, with emphasis on transition metal compounds such as permanganyl fluoride and nonclassical homoleptic carbonyl cations.

Poster Session J

Wednesday, September 8, 11:00

AB INITIO CALCULATIONS FOR INTENSITIES OF TEN ROTATION VIBRATION BANDS OF HYDROGEN SULPHIDE

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The hydrogen sulphide molecule's (H_2S) study is important because this molecule is a pollutant for troposphere. The observed transitions of fundamental bands ($\Delta v_1 + \Delta v_2 + \Delta v_3 = 1$) appear to be weaker than those in overtone bands ($\Delta v_1 + \Delta v_2 + \Delta v_3 = 2$)^a. Thus the main difficulty is to correctly reproduce the intensities of the ν_1 , ν_2 , and ν_3 weak bands from the first principles. The extremely shallow dipole moment functions close to the equilibrium geometry make, however, accurate calculations of this property function much more demanding than for H_2O or H_2Se .

The previous ab initio calculations of J.Senekowitsch and al.^b reproduced the overtone bands intensities in relatively good agreement with the observed corresponding bands intensities. But there is a great discrepancy between the calculated fundamental bands intensities and the observed corresponding bands intensities. In order to improve these results, we have done new ab initio calculations with another method than in ref[2]. The three-dimensional components of the dipole moment function were generated ab initio, using a finite perturbation by an external electric field and total energies from several CCSD-T approaches, the basis used is an augmented V5Z basis.

These calculations were done on a CRAY computer. Then we have fitted the *ab initio* dipole moment surfaces to the functional form suitable to perform fast calculations with Morse Oscillator Rigid Bender Internal Dynamic Model^c. One of CCSD-T approaches improves the overtone bands and another approach gives the fundamental bands in relatively good agreement with the observed corresponding bands. This presentation shows the results about ten rovibrational bands intensities and gives the dipole moment surfaces parameters for the two considered CCSD-T approaches.

^aL. Lechugat-Fossat et al., *Can. J. Phys.*, **62**, 1889-1923 (1984).

^bJ. Senekowitsch et al., *J. Chem. Phys.*, **90**, N.2, 783-794 (1989).

^cP. Jensen, *J. Mol. Spectrosc.*, **132**, 429-457 (1988).

AB INITIO POTENTIAL ENERGY SURFACE AND INTERNAL TORSIONAL-WAGGING STATES OF HYDRAZINE

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The three-dimensional potential energy surface describing the interaction of the large amplitude torsional and wagging motions of hydrazine has been determined from ab initio calculations. This surface has been sampled by a large set of grid points from the configurational space of the torsional and wagging coordinates.

The geometry optimization has been performed using the second-order Moller - Plesset perturbation theory with the basis set 6-311 + G(2df, 2p). At the optimized geometry, the single-point calculation of the electronic energy has been carried out using a larger basis set 6-311 + G(3dpf, 3pd).

The eigenvalue equation for the coupled torsional and wagging motions has been solved and obtained results has been compared to experimental data.

INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN THE CHIRAL MOLECULE CF_3CHF_2 : EXPERIMENT AND *AB INITIO* THEORY

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We have investigated the vibrational spectra and the underlying processes of intramolecular vibrational redistribution (IVR)^{a,b} of the chiral molecule tetrafluoroiodoethane (CF_3CHF_2) in experiment and *ab initio* theory, including the time dependent pseudo C_S -symmetry breaking mediated by anharmonic couplings^c.

The spectra^c were measured from the far infrared (20 cm^{-1}) to the visible (14200 cm^{-1}) range by interferometric Fourier transform infrared (FTIR) and photoacoustic techniques at resolutions between 0.004 and 1.0 cm^{-1} . Band positions and integrated band strengths of all fundamentals, numerous combination bands, and overtone transitions are reported. Assignments of fundamentals are made by comparison to harmonic vibrational frequencies, calculated *ab initio* (MP2/ C,H,F: 6-311G(d,p); I: LANL2DZ). The overtone transitions of the C–H chromophore are analyzed firstly by means of an effective Hamiltonian^{c,d,e} for the C–H stretch-bend Fermi resonance including the chiral C_S -symmetry breaking coupling^d, described by the anharmonic coupling constant $k'_{sab} = 30\text{ cm}^{-1}$. We present secondly detailed vibrational variational calculations of the overtone spectra of tetrafluoroiodoethane, based on three dimensional ($\nu_{CH} \times \delta_{CH,a} \times \delta_{CH,b}$) and four dimensional ($\nu_{CH} \times \delta_{CH,a} \times \delta_{CH,b} \times \nu_{CF}$) *ab initio* potential energy and dipole moment hypersurfaces^f. Explicit incorporation of the CF stretching mode ν_3 turned out to be sufficient and necessary to describe the experimental spectra properly up to excitation wavenumbers of 12000 cm^{-1} . Furthermore the unusually low values x_{sa} and x_{sb} found in the analysis of the experimental data using the 3D spectroscopic Hamiltonian are attributed to the perturbation of the pure CH chromophore by the CF stretching mode.

The femtosecond population dynamics of highly excited vibrational states is derived from the effective spectroscopic Hamiltonian in a first step and then

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^eH. R. Dübal, M. Quack, *J. Chem. Phys.* **81**, 3779 (1984).

^fJ. Pochert, M. Quack, M. Willeke, to be published.

compared to the wave packet and population dynamics evolving under the molecular Hamiltonian. In both cases different time scales for IVR processes within the CH modes and between CH modes and the CF frame mode ν_3 are found. The time evolution of states of formal A' and A'' symmetry shows a substantial mixing of the two subsets of states on a femtosecond time scale, i. e. chiral symmetry breaking.

SPECTROSCOPIC AND AB INITIO INVESTIGATION OF THE ν_{OH} OVERTONE EXCITATION IN TRANS-FORMIC ACID

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Fourier transform spectroscopy and intracavity laser absorption spectroscopy are used to record the absorption spectrum of formic acid at high spectral resolution, in the ranges of $2\nu_{\text{OH}}$ (6968.258 cm^{-1}) and $4\nu_{\text{OH}}$ ($13284.075 \text{ cm}^{-1}$) vibrational bands of the trans-rotamer, respectively. Numerous perturbations combined to a large line density prevent a complete vibration-rotation analysis to be performed. Some 689 transitions are identified in the first overtone band and vibration-rotation constants are determined for the ground and $\nu_{\text{OH}} = 2$ states by simultaneously fitting infrared and literature microwave data using a I^R Watsonian in A reduction. The band origin and upper state principal rotational constants are extrapolated for the $n = 4$ overtone band, and the validity of the predicted constants is validated by simulating the details in the observed band shape. Interpolation helped by literature data leads to similar results for the $n = 1$ and 3 bands in the series. All resulting trends along the $n\nu_{\text{OH}}$ excitation series are fully supported by precise effective ab initio calculations considering a one-dimension potential energy surface. The results of those calculations are detailed in terms of the mean nuclear structure in the excitation series, up to $n = 9$. The related calculated dipole moment surface allows the experimental $a : b$ subband intensity ratio in the series to be interpreted in terms of a decrease in the HOC angle.

**AB INITIO CALCULATIONS ON THE QUASILINEAR
MOLECULES ClCNO AND BrCNO**

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The molecular parameters of chlorofulminate, ClCNO, and bromofulminate, BrCNO, have been determined in large-scale *ab initio* calculations using the coupled-cluster method, CCSD(T), and basis sets of double- through quintuple-zeta quality. The potential energy functions for the large-amplitude ClCN/BrCN bending motion (the ν_5 mode) were determined to be strongly anharmonic. The barrier to linearity of the ClCNO chain was predicted to be 156 cm^{-1} , whereas that of the BrCNO chain was predicted to be 119 cm^{-1} . The rotation-bending energy levels for both molecules were then calculated using a semirigid-bender Hamiltonian. The effective rotational constants determined for various ν_5 states were found to be in excellent agreement with the recent experimental data.

MICROWAVE SPECTRUM, CONFORMATION, BARRIER TO
INTERNAL ROTATION ^{14}N QUADRUPOLE COUPLING
CONSTANTS, DIPOLE MOMENT AND QUANTUM CHEMICAL
CALCULATIONS FOR METHYL CARBAMATE

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The microwave spectrum of methyl carbamate ($\text{H}_2\text{NCO}_2\text{CH}_3$) has been investigated in the the 13.5 - 40.0 GHz spectral region at room temperature. One conformer was assigned. This rotamer has a symmetry plane (C_s symmetry) and two out-of-plane hydrogen atoms. The methyl and the carbonyl groups are in the *syn* conformation. The barrier to internal rotation of the methyl group is $4235.9(66) \text{ J mol}^{-1}$. The dipole moment is (in units of 10^{-30} C m) $\mu_a = 0.544(7)$, $\mu_b = 7.653(31)$ $\mu_c = 0$ (for symmetry reasons) and $\mu_{tot} = 7.672(31)$. The ^{14}N quadrupole coupling constants were found to be $\mathcal{X}_{aa} = 1.52(27)$ and $\mathcal{X}_{bb} = 3.51(15) \text{ MHz}$.

The microwave work has been assisted by *ab initio* computations at the HF/6-311++G**, MP2/6-311++G** (frozen core) levels of theory, as well as density theory calculations at the B3LYP/6-31G* level.

MICROWAVE SPECTRUM OF DEUTERATED METHANE AND WATER COMPLEX

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Rotational transitions of the deuterated methane and water van der Waals complex were observed using a pulsed nozzle Fourier transform microwave spectrometer. Six sets for the $J = 1 - 0$, $2 - 1$, and $3 - 2$ transitions were measured in the region between 7.8 and 23.2 GHz. These sets are explained based on the three states, A, E, and F, of the nearly free internal motion for deuterated methane and the two states of the exchange of two equivalent hydrogen atoms of water in this complex. The order of the A, E, and F states and the energy separation of the exchange motion of water observed for CD_4-H_2O was different from those for CH_4-H_2O ^a.

^aR. D. Suenram, G. T. Fraser, F. J. Lovas and Y. Kawashima *J. Chem. Phys.* **101**, 7230 (1994).

**TIME RESOLVED MMW/MMW DOUBLE RESONANCE
SPECTROSCOPY ON METHYL FLOURIDE:
OBSERVATION OF A K-CHANGING COLLISION PROCESS**

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We report our recent experiments to measure directly collisional relaxation rates of methyl flouride (CH_3F) in collision with Helium at low temperatures (2–20 K) using time resolved millimeter/millimeter wave double resonance spectroscopy and employing the collisional cooling technique. This system uses a BWO synthesizer and a ferrite waveguide switch to generate the pulsed pump radiation. The collisional relaxation can be monitored using a klystron based millimeter wave harmonic generator. We will discuss our current results for relaxation rates where we pump the $J = 2 \rightarrow 3$ transitions and probe the $J = 3 \rightarrow 4$ as well as the $J = 4 \rightarrow 5$ transitions of the methyl flouride molecule within the K -states 0,1 and 2. We will emphasize the observation of probe signals in a transition with $K = 2$ upon pumping a transition in $K = 1$. Since there are no dipole allowed radiative transfer processes between states with different K , we must assume K -changing collisions of methyl flouride with Helium to explain this. These data are compared with recent quantum scattering calculations using the MOLSCAT^b program in order to predict collision induced relaxation rates. We will also report theoretical studies which employ the solution of the Master equation for the population flow of a multilevel system in order to justify the analytical procedure we use to generate rate constants from the observed time dependent probe signals.

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^bJ. M. Hutson and S. Green, MOLSCAT Computer Code, Distributed by Collaborative Computational Project No. 6 of the Science and Engineering Research Council (UK)

MICROWAVE AND MILLIMETERWAVE SPECTRUM OF ACETIC ACID

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Acetic acid is of astrophysical interest, since several of its rotational transitions have been detected in interstellar space. It is also of theoretical interest because it is an example of a relatively near-oblate internal rotor molecule with the methyl top axis approximately perpendicular to the near symmetric top axis. The data set found in the literature has been augmented by new microwave and millimeterwave data obtained in different frequency ranges by different laboratories. The new measurements made in Lille cover the frequency range from 148 to 250 GHz using a broadband recording spectrometer. The NIST measurements have been performed between 78 and 118 GHz and between 360 and 365 GHz using the rapid scan spectrometer followed by high resolution measurements using conventional step-scanned BWO's. Approximately 40 transitions from 10 to 24 GHz, involving $J \geq 6$, $K_a \geq 5$ and $K_c \geq 4$, and $v_t = 0$ where v_t is the torsional quantum number, were carried out with the Fourier transform spectrometer at NIST. Finally, a number of measurements in the frequency range from 60 to 155 GHz were performed in Kharkov. All those new measurements as well as the previous ones published earlier were included in a global fit involving the two first torsional states, $v_t = 0$ and 1 and $J \leq 20$. The RAM approach, successfully used with acetaldehyde in the past is applied to provide a weighted standard deviation of 1.2 for 1146 lines using 26 parameters. The fit for the ground state $v_t = 0$ is excellent whereas the $v_t = 1$ data set still needs to be cleaned up and completed.

THE ROTATIONAL SPECTRUM OF NF_3 IN THE VIBRATIONAL STATE $\nu_4=1$

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We have investigated the rotational spectrum in the isolated degenerate vibrational level $\nu_4=1$ of the symmetric top molecule NF_3 . Rotational transitions following the $\Delta J = 1, \Delta K = 0$, selection rule have been observed in Lille in the millimeter- and submillimeterwave range with J'' values from 6 to 20 and K up to 20. Direct l -type resonance transitions following the selection rules $\Delta J = 0, \Delta k = \Delta l = \pm 2, \Delta G = \Delta |k - l| = 0$ with J values from 7 to 18 and G up to 9 as well as the $J = 1 \leftarrow 0$ transition have been measured in Kiel using microwave Fourier transform (MWFT) spectroscopy.

Splittings due to nuclear quadrupole coupling of the ^{14}N nuclear spin $I = 1$ were observed for several transitions recorded with MWFT spectroscopy.

The data were analyzed taking into account rovibrational and hyperfine interactions simultaneously using three different sets of parameters. These correspond to three reduced forms of the effective Hamiltonian and the unitary equivalence is demonstrated.

Due to an accidental degeneracy, the rotational constant C_4 could be determined. The obtained value leads to an improved calculation of the structure which is in good agreement with ab initio calculations.

THE MICROWAVE SPECTRA OF BENZOTHAZOLE AND 2-METHYLBENZOTHAZOLE

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In order to investigate the influence of the substituents on the ring system of thiazole containing compounds we measured the rotational spectra of benzothiazole and 2-methylbenzothiazole. For the measurements we used a molecular beam Fourier transform microwave (MB-FTMW) spectrometer in the range from 3 to 26.5 GHz.

For both molecules we were able to assign the rotational spectrum in the vibrational ground state and to determine the rotational constants, the quartic centrifugal distortion constants, and the quadrupole coupling constants.

In addition to the splitting caused by quadrupole coupling of the ^{14}N nucleus of 2-methylbenzothiazole we observed a splitting into two line components due to internal rotation of the methyl group. Assuming mainly V_3 contribution, the internal rotation splitting allowed us to determine the internal rotation barrier.

Via the quadrupole coupling constants we will compare the electronic environment of the nitrogen nucleus in the thiazole^a, the monomethylthiazoles^b ^c benzothiazole, and 2-methylbenzothiazole to see systematic effects of substituents on the thiazole ring.

Further, we will show the difference between the barrier height of 2-methylthiazole^d and 2-methylbenzothiazole.

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HIGH RESOLUTION SPECTRUM AND ROVIBRATIONAL ANALYSIS OF THE ν_2 / ν_5 DYAD OF D_3SiF NEAR 700 cm^{-1}

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The ν_2 (A_1 , 710.157 cm^{-1}) and ν_5 (E , 701.717 cm^{-1}) fundamental bands of $D_3^{28}Si^{37}F$ have been studied by FTIR spectroscopy with a resolution of $2.4 \times 10^{-3}\text{ cm}^{-1}$. We assigned 1644 lines for the parallel band ($J_{max}=50$, $K_{max}=21$), 4330 for the perpendicular band ($J_{max}=52$, $K_{max}=27$), and in addition 671 perturbation-allowed transitions ($J_{max}=50$, $K_{max}=12$). The nearly degenerate $\nu_2=1$ and $\nu_5=1$ states are linked by ($\Delta K = \pm 1$, $\Delta l = \pm 1$) and ($\Delta K = \pm 2$, $\Delta l = \mp 1$) interactions while the $l_5 = \pm 1$ levels of ν_5 interact also by $l(2,-1)$, $l(2,2)$ and $l(2,-4)$ interactions.

A first model with 36 free parameters, taking into account all these resonances through a non linear squares program, gave standard deviations of $1.56 \times 10^{-4}\text{ cm}^{-1}$ for 6120 non zero-weighted IR data and 138 kHz for 8 MW data from the literature. A second model, in which the main Coriolis term was constrained to a force field value, used 37 parameters and gave similar standard deviations.

A new determination of the A_0 and D_K^0 ground state parameters was performed by two methods: either using differences between 'forbidden' transitions differing by 3 in K or letting A_0 and D_K^0 free in the global fit. The values obtained are fully compatible with those obtained previously by the 'loop method'.

HIGH-RESOLUTION FOURIER TRANSFORM INFRARED
SPECTROSCOPY AND ANALYSIS OF THE ν_3
FUNDAMENTAL BAND OF P_4

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In spite of its fundamental importance as a well-known metastable modification of an ubiquitous, common element of technical importance the structure and the spectroscopic parameters of the free P_4 molecule (white phosphorus) are not known at a state-of-the-art level.

We present the first high-resolution infrared absorption study of the ν_3 fundamental of P_4 ^a. Measurements were performed using a Bruker 120HR interferometer with a resolution (1 / maximum optical path difference) adjusted to $6 \times 10^{-3} \text{ cm}^{-1}$. The spectrum was recorded at the lowest temperature feasible, 413 K.

This analysis was performed using the STDS (Spherical Top Data System) software developed in Dijon. We have resolved the Q branch and the tetrahedral fine structure of the J clusters in the P and R branches and unambiguously determined several spectroscopic parameters up to third order that enable a satisfactory reproduction of the experimental spectrum by a simulation. The band center lies at 466.286 cm^{-1} . With the approximation $(B\zeta)_3 = -B_0/2$, we found that the ground state bond length is $r_0 = 219.58 \text{ pm}$.

Our values are in agreement with the *ab initio* structural parameters for P_4 ^{b,c} but significantly differ from a value obtained in a previous Raman study^d.

^aV. Boudon, E.B. Mkadmi, H. Bürger, and G. Pierre, *Chem. Phys. Lett.*, *In press* (1999).

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^cB. Persson, P. Taylor, and T. Lee, *J. Chem. Phys.* **107**, 5051 (1997).

^dN. Brassington, H. Edwards, and D. Long, *J. Raman. Spectrosc.* **11**, 346 (1981).

**FOURIER TRANSFORM HIGH RESOLUTION STUDY OF BAl
MOLECULE: THE FIRST SEVEN LOW-LYING
ELECTRONIC STATES**

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Near-infrared and visible spectra of BAl molecule, obtained from the chemiluminescent reaction $Ba + I_2$ and also by Laser Induced Fluorescence (LIF), were recorded by using Fourier Transform Spectroscopy (FTS). The LIF spectra were obtained from forty five exciting laser lines provided by Ti:Sa, Ar⁺, Kr⁺, dye lasers and second harmonic of Sa:Ti laser lines. Ten band systems involving the first seven electronic states were observed and analysed. More than 7 000 lines were assigned and in the final analysis the obtained data set was combined with previous data of C-X band system, taken from C. A Leach *et al.*, *J. Mol. Spectrosc.*, **153**, 59-72. The derived molecular constants set reproduces the analysed transitions with a statistical error less than $3.2 \times 10^{-3} \text{cm}^{-1}$.

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**EXTENDED ASSIGNMENTS, VIBRATIONAL COUPLING,
AND MODELING FOR THE C-O STRETCH BAND OF CH₃OH**

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The Fourier transform spectrum of the CO-stretching fundamental of CH₃-OH has been re-examined at higher pressure and path length than heretofore in a study of the lower modes over the 930-1400 cm⁻¹ region. With the increase in spectral sensitivity, it has been possible to assign a significant number of new subbands for torsionally excited $\nu_t = 1$ and $\nu_t = 2$ substates, plus some high-K subbands for the $\nu_t = 0$ torsional ground state. Assignments have also been extended to higher J for most of the previously known subbands. We have observed a number of new J-localized resonances arising from level-crossings with other torsion-vibration modes. The partner levels have been identified and the interactions characterized for some of the resonances, while others remain mysterious. We are exploring the extent to which the unperturbed CO-stretching levels can be modelled by an effective Hamiltonian of the multi-parameter type used successfully to fit the ground state. So far, 1620 lines have been fitted with a weighted standard deviation of 100 corresponding to a mean residual of approximately 0.02 cm⁻¹, still some distance from experimental uncertainty.

**THE BANDS OF CH_4 BETWEEN 5900 cm^{-1} AND 6200 cm^{-1} :
 $2\nu_3$ AND $2\nu_2 + \nu_3$**

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The rovibrational levels in methane are grouped in vibrational polyads. The infrared spectrum associated to the three first excited polyades of methane (dyad : $6 - 10\ \mu\text{m}$, pentad : $3 - 6\ \mu\text{m}$ and octad : $2 - 3\ \mu\text{m}$) can be considered as very well known : positions and intensities. The upper polyad called tetradecad ($1.6 - 2\ \mu\text{m}$) is composed of 14 vibrational levels (of 2, 3 and 4 quanta) altogether made up of 60 sublevels.

Among the 14 bands of the tetradecad system, only two of them, namely $2\nu_3$ and $2\nu_1$, were studied before separately as isolated bands. In these two cases, it appears that the isolated band model was not adequate to account for strong interactions between neighbouring levels. The challenge of our work is to analyze all fourteen bands in polyad scheme.

The main experimental data are one jet-cooled spectrum recorded by R. Georges et al. at the Université Libre de Bruxelles^a and four infrared spectra recorded by L.R. Brown at the Keat Peak National Observatory. In addition, we have at our disposal some data of infrared-infrared^{b, c} and Raman-Raman double-resonance^d experiments.

The infrared spectrum around 6000 cm^{-1} includes the allowed transitions of the $2\nu_3$ band and a lot of non identified lines of weaker strength. It has been possible to assign some of these lines to rovibrational forbidden transitions of the $2\nu_3$ band and some others to rovibrational allowed transitions of the $2\nu_2 + \nu_3$ band.

The well understanding of the spectrum of the bands $\nu_1 + \nu_3$ and $\nu_2 + \nu_3 + \nu_4$ in the same region represents the next step of this work to reproduce the whole spectrum of the tetradecad. The identification of these two bands is in progress.

^aR. GEORGES, M. HERMAN, J.-C. HILICO, AND O. ROBERT, *J. Mol. Spectrosc.* **187**, 13-20 (1998).

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^dR. Z. MARTINEZ, B. BERMEJO, J. SANTOS, J.-P. CHAMPION, AND J.-C. HILICO, *J. Chem. Phys.* **107**, 4864-4874 (1997).

A COMBINED ANALYSIS OF THE ν_9 BAND AND THE FAR-INFRARED TORSIONAL SPECTRA OF ETHANE

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Fourier transform measurements of the lowest frequency degenerate fundamental band of CH_3CH_3 ($\nu_9 = 1 \leftarrow 0$) in the $12\text{-}\mu\text{m}$ region together with far-infrared torsional spectra have been analyzed to investigate vibration-torsion-rotation effects in a symmetric top molecule. Several spectra of the ν_9 band were recorded at different experimental conditions with apodized apparatus functions of about 0.002 cm^{-1} . Although the intrinsic tunneling splitting in each ($J' \leftarrow J''$) doublet in the ν_9 band is predicted to be of the order of 0.002 cm^{-1} , in some cases the observed splitting for an intermediate J'' of 20 is several times this value. In more favourable cases, splittings of order of 0.25 cm^{-1} have been observed. These splittings are caused primarily by the Coriolis interaction between the torsional stack of levels $\nu_4 = 0, 1, 2, \dots$ for ($\nu_9 = 1$) and the corresponding stack for the ground vibrational state. Because of a near-degeneracy between the upper level in the ν_9 band and its interacting partner, ($\nu_9 = 0, \nu_4 = 3$), the ($l = -1; K = 17, \sigma = 0$) torsion-rotation series is resonantly perturbed. For this case, perturbation-allowed ($\nu_6 = 3 \leftarrow 0$) torsional transitions have been identified. Here $\sigma = 0, 1, 2$, 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 a symmetry adapted effective Hamiltonian which has been used for analyses of similar spectra in methyl silane and CH_3CD_3 . Two Coriolis parameters were determined; the experimental value of $\tilde{\zeta}_9^z = 0.261(12)$ is in good agreement with the calculated value of 0.25, whereas the experimental value of $\tilde{\zeta}_{4,9}^x = 0.2269(12)$ is about 3 times smaller than the calculated value of 0.60.

DIODE LASER SPECTROSCOPY OF CH₂⁸¹BrF IN THE ν_4 REGION

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Bromofluoromethane is a simple molecule which has been studied very little in the microwave as well as in the infrared region. Very recently we reported an extensive vibrational analysis of its gas-phase infrared spectrum^a. All the fundamentals and many overtones, combination and hot bands were recognized leading to an almost complete set of anharmonicity constants. In order to perform a reliable interpretation of the absorption bands, the assignment was also assisted by the analysis of enriched spectra of ^{79/81}Br isotopomers synthesized in our laboratory.

We have now recorded the high resolution infrared spectrum of CH₂⁸¹BrF in the ν_4 band region and the present communication is devoted to the results of this investigation. The molecule belongs to the C_s point group and the ν_4 vibration of A' symmetry, approximately representing the C-F stretching mode, yields a very strong **a/b**-hybrid band with prevalent **a**-type character. The spectra were obtained with a TDL spectrometer, in the range 1002-1120 cm⁻¹, at a resolution of about 0.002 cm⁻¹ and at 240 K to reduce the hot band contribution. Since the molecule approaches to a prolate symmetric top ($\kappa = -0.986$), the structure exhibits patterns characteristic of parallel (**a**-type) and perpendicular bands (**b**-type).

More than 6600 transitions ($J \leq 98$, $K_a \leq 23$) were assigned to provide the rovibrational constants of the essentially unperturbed $\nu_4 = 1$ state. The final results were obtained using the Watson's A-reduced Hamiltonian in the I'-representation. In the course of the analysis, the ground state parameters were improved and extended to the sextic centrifugal distortion constants by applying the weighted GSCD method.

The details of the analysis will be presented.

^aA. Baldacci, A. Baldan, A. Gambi and P. Stoppa, *J. Mol. Struct.*, accepted (1999).

THE MYSTERY OF A BAND VANISHING UPON ISOTOPIC SUBSTITUTION. THE CASE OF THE $\nu_3 = 1$ STATE OF FCLO_3

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Meguellati, Graner, Burczyk, and Bürger reported in their recently published paper^a on $\nu_3(A_1)$ bands of the $^{35,37}\text{Cl}$ and $^{16,18}\text{O}$ isotopomers of FCLO_3 that the ν_3 bands, which, although weak, could be well observed for the ^{16}O isotopomers, disappear completely in the spectra of the ^{18}O isotopomers. Several possible explanations of this disappearance are proposed and analyzed in this contribution. The most likely explanation is that it is just a coincidence among the intensity parameters which is responsible for a very low value of a dipole moment derivative and a weak Fermi resonance with the ($\nu_6 = 2, l = 0$) state may also participate in the final total wipeout of the band. It is believed that the last mechanism can be of more general interest.

^aF. Meguellati, G. Graner, K. Burczyk, and H. Bürger *J. Mol. Spectrosc.* **185**, 392, 1997

**ROTATIONAL TRANSITIONS IN HOT EMISSION HDO
SPECTRUM IN THE 400-850 cm^{-1} REGION AND HIGH- J , K_a
ENERGY LEVELS OF THE (000) AND (010) STATES**

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The emission spectrum of water has been recorded at high resolution in the 400-850 cm^{-1} region. The spectrum was recorded at 1100K temperature with pressure \times pathlength product $p \times l = 16\text{mbar} \times 60\text{cm}$. About 600 lines of the (000)-(000) band and 400 lines of the (010)-(010) band of HDO were assigned, many of them for the first time.

These data allowed us to obtain the energy levels of the (000) and (010) states of HDO molecule with high values J and K_a . The results of the energy fitting for both states using G-function approach are presented.

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EXPERIMENTAL AND THEORETICAL STUDY OF LINE
MIXING IN METHANE SPECTRA.
THE Q BRANCH OF THE RAMAN ν_1 BAND
PERTURBED BY He AND Ar

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The shape of the ν_1 Q branch of CH₄ perturbed by Ar and He at room temperature has been studied. Stimulated Raman Spectroscopy (SRS) experiments have been made in the 2915 - 2918 cm⁻¹ spectral region for total pressures from 0.4 to 70 atm and mixtures of 5% CH₄ with He and Ar. Analysis of the spectra demonstrates that the shape of the Q branch is significantly influenced by line mixing and much narrower than predicted by the addition of individual line profiles. A model is proposed, where the relaxation matrix is constructed starting from semiclassical state-to-state rates, for the prediction and analysis of the spectral shape. Two empirical constants which account for the shift and broadening of the branch due to vibrational effects are introduced and their values are determined from fits of measured spectra. Comparisons between measurements and results computed accounting for and neglecting line mixing are made. They prove the quality of the approach which satisfactory accounts for the effects of pressure both at low densities (where rotational transfers are dominant) and high densities (where the profile is determined by vibrational contributions). It is shown that collisions with He and Ar lead to different behaviors at elevated pressure. The influence of the perturbation introduced by the Fermi coupling between the ν_1 and $\nu_2 + \nu_4$ levels is discussed and the rotational and vibrational contributions to the spectra shape are pointed out.

MEASUREMENT OF PRESSURE SHIFTING OF ONE METHANE LINE IN THE 1.6 μm REGION

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Pressure-induced line shift coefficients of methane absorption lines are very important for infrared transmission and radiance calculations in the terrestrial as well as planetary atmospheres.

A diode laser spectrometer with a room-temperature diode laser near 1.65 μm is used for the detection of CH_4 in air with high sensitivity and accuracy. To provide the measurements at the different altitudes the pressure effects on the analytical spectral line parameters have been measured.

In this paper the diode laser spectrometer with a Helmholtz photoacoustic resonator cell was applied to detail measurements of shift coefficients of a CH_4 absorption line ($\text{R}(3)$, $2\nu_3$ band) perturbed by N_2 , O_2 , and air pressure.

The experimental data on the shift of the absorption line under study in binary mixtures were used to check up the additivity of the binary collisions $\text{CH}_4\text{-N}_2$, $\text{CH}_4\text{-O}_2$, to the shift of the same line due to air pressure.

LINE PARAMETERS OF $^{12}\text{C}^{16}\text{O}_2$ IN THE 1.2-1.3 μm REGION

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The 7000-8500 cm^{-1} region of CO_2 has been investigated using the high resolution FT spectrometer of LPPM in Orsay. The two strongest bands in this region are the $\nu_1 + 3\nu_3$ dyad bands centered at 8192 and 8294 cm^{-1} . A complete set of line parameters of the 10031-00001 and 10032-00001 bands, line positions and intensities, self-broadening and self-induced lineshifts coefficients, has been obtained. In addition, line intensities in the 40013-00001 and 40014-00001 bands have been measured in order to compare our results with those of Giver et al¹. Results of a global fit of line positions and line intensities of $^{12}\text{C}^{16}\text{O}_2$ using the method of effective operators have been recently reported^{2,3}. Our line intensities measurements have been included in a new fit of effective dipole moment parameters to all available experimental data in this spectral region. The corresponding calculated line intensities of the 10031-00001 and 10032-00001 bands are compared with the experimental ones. The main interest of this research lies in the importance of the CO_2 emission windows to determine the composition and cloud structure of the lower Venus atmosphere.

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**PRESSURE-SHIFT AND PRESSURE-BROADENING IN THE
 $\nu_1 + 3\nu_3$ BAND OF ACETYLENE IN THE NIR RANGE**

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We have developed a spectrometer based on a Ti:Sa Autoscan laser and used it to determine the line broadening γ and the line shift δ coefficients for the $\nu_1 + 3\nu_3$ band of $^{12}\text{C}_2\text{H}_2$ with J -values ranging from 0 to 22. The absorption cell was a White-type multiple-pass cell with a path length of about 64 m and was filled with acetylene up to 500 torr. An optoacoustic cell, with a low and constant acetylene pressure, was used simultaneously to provide reference measurements in the shift experiments. The broadening and shift coefficients for self-collision and collision by Ar and Xe perturbers are presented. The observed line shape at high acetylene pressure was fitted with the Voigt profile. The Galatry and Rautian/Sobelman models were used to account for line-narrowing effects at lower pressure. The collisional lineshift measurements present a significant difference from the overall J -dependence of the band for the upper $J=18$ rotation level. We discuss this unexpected result in terms of interaction between *inter-* (collisional processes) and *intra-* (Coriolis-type coupling with a nearby state) molecular dynamics.

THE VIBRATIONAL ENERGY PATTERN IN ACETYLENE ISOTOPOMERS

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The vibrational energy pattern in acetylene was investigated over the last years for four isotopomers : $^{12}\text{C}_2\text{H}_2$, $^{13}\text{C}_2\text{H}_2$, $^{12}\text{C}_2\text{D}_2$ and $^{12}\text{C}_2\text{HD}$ [1-4]. An effective Hamiltonian was built for each molecule, based on the clustering of the energy levels in polyads. According to the theoretical model developed by Kellman [5] each cluster or polyad is characterized by a set of dynamical constants of motion directly related to the set of anharmonic resonances affecting the vibrational pattern of the molecule. The experimental vibrational levels were gathered and fitted simultaneously for each isotopomer, yielding to rotation-vibration parameters. The rms of the fit was always less than 1 cm^{-1} . In this poster, the parameters will be discussed. The experimental rotational constants of these four isotopomers of acetylene will be used to update the equilibrium bond lengths in acetylene.

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COLOGNE SIDEBAND SPECTROMETER FOR THz APPLICATIONS (COSSTA)

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The Cologne sideband spectrometer allows high resolution THz spectroscopy with high accuracy. It consists of an optically pumped far infrared ring laser and a broadband tunable backward wave oscillator (BWO) as sideband source. Since the BWO is phase locked to a rubidium reference, we were able to develop an automatic frequency control (AFC) for our laser system with a relative frequency accuracy of about 1-2 kHz. The sideband beam with a power of up to 500 nW (estimated from the optical response of the detector) is generated by a whisker contacted Schottky diode and separated by a grating from the other beams. The half power bandwidth (HPBW) is limited by the laser system. In comparison to a linear laser, a ring laser has the advantage that only one velocity class is pumped, resulting in a smaller HPBW. The absolute frequency accuracy of COSSTA is about 5 kHz. This offers the possibility of very precise and highly resolved measurements at 1.8 - 2.0 THz.

We will present spectroscopic results (e.g. CO, D₂S₂, NH, NH₂, NH₃) and a detailed description of the spectrometer. An optimization of the sideband power, the spectrometer sensitivity and the frequency range is under progress.

HIGH RESOLUTION ANALYSIS OF THE $K_a = 0 \leftarrow 1$ SUBBANDS OF THE FUNDAMENTALS ν_3 AND ν_6 OF $(\text{HF})_2$

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Hydrogen bond quantum dynamics remains among the major questions in chemical physics. The dimer of hydrogen fluoride, $(\text{HF})_2$, is a prototype system with H-bonding and has been extensively investigated. Four of the six fundamentals of this very flexible molecule are expected below 600 cm^{-1} . The far-infrared spectrum therefore represents a particularly rich source of information on structure and dynamics of this molecule. Earlier investigations of the far-infrared spectrum could identify the $K_a = 1 \leftarrow 0$ transition of the ν_6 fundamental [1] as well as excited K_a levels of ν_0^b , [3], ν_5 [4] and an approximate value of ν_4 [5]. However, many structures in the far infrared spectrum remained unexplained. In particular the band centers of the symmetric bending (conrotatory bending) fundamental ν_3 as well as the $K_a = 0$ level of the out-of-plane bending (torsional) fundamental ν_6 are not experimentally known until now. These data are of utmost importance for a detailed comparison of experiment and theory [6-8].

We performed new measurements of the far-infrared spectrum of $(\text{HF})_2$ in the region $125 - 680 \text{ cm}^{-1}$ on our BOMEM DA002 high resolution FTIR spectrometer. We used a coolable *White type* long path cell from *Portmann Instruments AG, Switzerland*, which has been designed specifically to be resistant to HF. In a typical measurement, the sample pressure chosen was 20 mbar and the cell temperature 243 K. Under these conditions, the spectra taken at a resolution of 0.01 cm^{-1} were pressure limited.

By means of combination differences based on ground state constants from ref. [3], we were able to definitely assign both tunneling components of a subband with Q-branch structures near 380 cm^{-1} to the $K_a = 0 \leftarrow 1$ subband of the fundamental ν_6 . We recognized a further subband near 450 cm^{-1} with identical lower states as in the case before. Calculations [5-9] strongly support the assignment of this second subband to the $K_a = 0 \leftarrow 1$ subband of ν_3 . We have therefore been able to determine experimentally the centers of the fundamentals ν_3 and ν_6 , which represent valuable test data in conjunction with the modelling of the vibrational-tunneling dynamics ($J=0$ problem) of

this molecule [5–9].

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CURVILINEAR INTERNAL VALENCE COORDINATE HAMILTONIAN FOR AMMONIA

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A new six-dimensional vibrational Hamiltonian based on curvilinear internal valence coordinates is presented for ammonia. The inversion coordinate adopted is similar to the often used out-of-plane bending coordinate for planar XY_3 -type molecules [A. R. Hoy, G. Strey, and I. M. Mills, *Mol. Phys.* 24, 1265 (1972)]. Conventional symmetrized internal coordinates are employed for the other vibrational degrees of freedom. The redundancy relation involving the inversion coordinate and the three valence angle coordinates is expanded around the planar configuration to provide coordinate transformations between symmetrized and unsymmetrized coordinates.

A HINDERED-ROTOR MODEL HAMILTONIAN FOR HCN/CNH

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Effective (or model) Hamiltonians, obtained either from canonical perturbation theory or from a fit to experimental or ab initio energy values, are of great help in understanding the highly excited vibrational dynamics of small molecules, because of the remaining good quantum numbers which are explicitly contained in their expressions. For example, it has been shown recently, that Fermi resonance Hamiltonians lead to a clear picture of the dynamics of HCP (up to 80% of the energy of the saddle point between the HCP and CPH configurations) and of HOCl (up to 98% of the energy of the dissociation into HO+Cl). The Fermi resonance Hamiltonian, however, can only be used for molecules with a single equilibrium configuration. It is shown here, that models built on the hindered rotor Hamiltonian are powerful tools for the study of the dynamics of molecules with a multi-well potential energy surface. The prototypical HCN/CNH molecule is given as an example, and it is shown that the hindered rotor Hamiltonian reproduces accurately the ab initio energy values and wave functions calculated previously up to and above the isomerization barrier [1]. Most important, however, is the fact that this model allows for two good quantum numbers, which simplifies drastically the discussion of the highly excited vibrational dynamics in terms of classical bifurcations and Periodic Orbits.

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**HIGH RESOLUTION SPECTROSCOPY OF THE
 $A^1\Sigma^+ - X^1\Sigma^+$ SYSTEM OF LiH**

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We have performed a sub-Doppler experiment involving a molecular beam of LiH and cw UV radiation around 350 nm produced by doubling a Ti-Sapphire source in an external cavity. This allowed to record more than 400 lines of the $A^1\Sigma^+ - X^1\Sigma^+$ system of the two isotopomers ^6LiH and ^7LiH . The resolution is 0.005 cm^{-1} . The accuracy provided by the calibration on the iodine absorption spectrum is of the order of 0.005 cm^{-1} . Accurate spectroscopic constants will be presented at the conference.

**ELECTRONIC GROUND AND EXCITED STATE
SPECTROSCOPY OF C₆H AND C₆D**

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Rotational transitions in the X²Π ground state of C₆H and C₆D have been measured by a Fourier transform microwave and millimeter wave spectrometer. In total more than 150 individual lines in the ²Π_{3/2} and ²Π_{1/2} rotational ladders have been observed, which allows an accurate determination of the rotational, fine structure, lambda-doubling and hyperfine coupling constants, using a standard effective Hamiltonian for a linear molecule in an isolated ²Π state. The molecular ground state constants are used to characterize the rotationally resolved origin band of the astronomically relevant ²Π ← X²Π electronic transition, recorded by cavity ring down spectroscopy in a pulsed supersonic slit jet plasma. From this experiment, spectroscopic constants for the upper electronic state are determined. The poster will focus on the electronic spectroscopy.

HIGH RESOLUTION INFRARED SPECTROSCOPY OF IONIC COMPLEXES

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A sensitive and generally applicable technique for infrared high resolution spectroscopy of weakly bound ionic complexes is presented. The method is based on direct absorption of tunable diode laser radiation in an adiabatically cooled plasma. The plasma is generated by electron impact ionization of gas that is expanded supersonically through a long and narrow slit. The properties of the electron beam allow a fast and effective production modulation. Online monitoring by a quadrupole mass spectrometer yields direct information on the plasma characteristics. The technique is demonstrated for several ionic complexes, varying from N_4^+ and $N_2 \cdot H^+ \cdot N_2$ by exciting the anti-symmetric stretch, to $Ar-HN_2^+$ (NN and NH stretch) and $Ar-HCO^+$ (CO stretch) by exciting vibrational modes of the chromophore.

THE STABLE CONFIGURATIONS OF $(H_2O)_n(HF)_m$ COMPLEXES IN THE ATMOSPHERE

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The main stages of the nuclear fuel cyclic (NFS) are observed. Main chemical processes in the atmosphere involving the uranium fluorides and oxifluorides have been studied as well as influence of these processes on the vibrational spectra of the compounds. The HF molecule is formed by the interaction of UF_6 molecule and its hydrolysis products with water vapor. It is shown that the interaction of H_2O and HF molecules results in formation of structurally nonrigid molecular complexes $(HF)_n(H_2O)_m$. The interaction between H_2O and HF molecules is dominated by hydrogen bonding. The general spectral and structural trends by the formation of these complexes were studied. Structural parameters were found from HF/6-31G* ab initio geometry optimization. Vibrational frequencies were calculated from Newton-Raphson/3-21G ab initio optimization routine of second derivatives of the potential. Electronic excitation energies were calculated from ROHF/4-31G ab initio level of theory. The analysis of spectral features of complexes such as absorption band shifts has been done.

ABSORPTION SPECTROSCOPY OF THE GeH₂ RADICAL NEAR 585 nm

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The absorption spectrum of the germylene radical in the 585 nm region has been recorded by Intracavity Laser Absorption Spectroscopy. The radical has been produced in a continuous discharge in a flowing mixture of GeH₄ (5%) in argon. The sample of germane contains Ge in natural abundance, thus all five isotopes of germylene are contributing to the absorption spectrum. In fact, the typical pattern corresponding to the isotopic mixture was used as a clue for the identification of spectral features.

This spectral region corresponds to the first excitation of the bending in the first excited electronic state *i.e.* to the $A^1B_1(0, \nu_2 = 1, 0) - X^1A_1(0, 0, 0)$ transition. As far as we know, only one rotational line of this band had been previously observed by LIF and assigned to $^pP_1(1)^a$. Although we could not observe this line in our spectra, we found and assigned the $^pQ_1(J)$ and $^rQ_0(J)$ series, with $J = 1 - 10$. The appearance of the spectrum is quite similar to that of the central region of the $A^1B_1(0, 0, 0) - X^1A_1(0, 0, 0)$ of SiH₂, which we have studied recently^b. In fact, a few of the observed lines of GeH₂ seem to be affected by a weak perturbation, similarly to what we found for SiH₂. The perturbation does not prevent the assignment, but produces a deviation of up to 0.05 cm⁻¹ in the corresponding line positions.

Excluding the perturbed lines, we have refined the rotational constants of the excited state, keeping fixed the values of the ground state from the bibliography^a. As a consequence of an important increase of the bond angle, the A rotational constant varies largely from the value of the ground electronic state, and also differs from that of the first vibrational state in the A^1B_1 electronic state under study. From the values of the, α_2^A , α_2^B and α_2^C constants obtained from the present results and the rotational constants of the $A^1B_1(0, \nu_2 = 0, 0)$ ^a, the equilibrium geometry of the electronic state has been determined.

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STATE-TO-STATE ENERGY TRANSFER IN
ELECTRONICALLY EXCITED NH_2 , OBSERVED WITH TIME
RESOLVED FOURIER TRANSFORM EMISSION
SPECTROSCOPY IN THE VISIBLE

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Collisions and relaxation processes are important in chemical reactions, particular in atmospheric chemistry. For a complete understanding of such processes the knowledge of all quantum numbers of the states involved is desired. State-resolved collision experiments provide an excellent possibility to explore details of the collision mechanism and internuclear potentials. Such investigations are possible in electronically excited states if a dye laser is used to label exactly one initial rovibrational level. Collisional energy transfer to other rovibrational levels of this state can be observed from their time dependent fluorescence. Investigations on state-to-state energy transfer on polyatomic molecules are of particular interest since there is no unique relation between rotational energy and angular momentum.

In our experiment NH_2 is produced by photodissociation of NH_3 using 193 nm radiation. Due to a conical interaction between two potential surfaces of the dissociating NH_3 , NH_2 is generated as well in its ground $^2\text{B}_1$ as in its excited $^2\text{A}_1$ state, with high rotational excitation around its a axis $N = K_a \geq 12$. After a short delay, ground state NH_2 -molecules are excited to a specified rovibrational level in the $\tilde{\text{A}}$ -state. Collisions lead to a transfer of population from the initial to other levels. The dispersed fluorescence is recorded using time-resolved Fourier transform emission spectroscopy (TR-FTES).

The predominant collision partner is identified by varying the power of the dissociation laser, which results in a change of the composition of the gas ensemble. Propensity rules for the observed collisions are determined, from which one concludes the leading order of the intermolecular potential.

By increasing the time delay between the dissociation and exciting laser, rovibrational levels with lower rotational excitation ($N \leq 10$) are reached, which are of particular interest since the NH_2 molecule is quasi-linear for this state and shows a coupling between electronic and vibrational angular momentum (Renner-Teller effect), while levels with high rotational excitation show a large centrifugal distortion in the light NH_2 molecule.

We will present cross sections for inelastic collisions between NH_2 and NH_3 .

HIGH RESOLUTION RAMAN SPECTRUM OF $^{12}\text{C}_2\text{D}_2$: THE ν_2 FUNDAMENTAL AND ASSOCIATED HOT BANDS

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The Raman spectra of the Q branch of the ν_2 band of $^{12}\text{C}_2\text{D}_2$ and associated hot bands ($\nu_2 + \nu_4 - \nu_4$, $\nu_2 + \nu_5 - \nu_5$, $\nu_2 + 2\nu_4 - 2\nu_4$, $\nu_2 + 2\nu_5 - 2\nu_5$, $\nu_2 + \nu_4 + \nu_5 - \nu_4 - \nu_5$ and $2\nu_2 - \nu_2$) have been recorded with an instrumental resolution of about $3 \times 10^{-3} \text{cm}^{-1}$. All of them except $2\nu_2 - \nu_2$ have been recorded using a high resolution inverse Raman technique. For $2\nu_2 - \nu_2$, this technique has been combined with Stimulated Raman pumping in order to populate the $\nu_2 = 1$ state. Band by band analysis of the assigned transitions has been performed yielding precise values of spectroscopic parameters for the vibrationally excited states, including the *l* – *type* interaction constants. The energies of the levels for the ground and the bending states were calculated by means of the molecular constants reported in the literature^a. Standard deviations of the order of $2.0 \times 10^{-4} \text{cm}^{-1}$ have been obtained. Our results are compared to those available in the literature.

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**LOOSELY BOUND STATES OF A TRIATOMIC MOLECULE,
INFLUENCE OF THE LONG RANGE ELECTROSTATIC
INTERACTIONS ON THE DENSITY OF LEVELS**

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We report our recent theoretical investigations about the effect of long range interactions on the eigenstates of a triatomic molecule near its dissociation threshold. Our previous LIF and LIDFS experimental results on NO₂ show, within the last 20 cm⁻¹ below the dissociation threshold, an unexpected and sudden increase of the density of states and anomalous rotational selection rules.

We attribute these effects to the long range interactions (involving dipole, quadrupole and dispersion terms) between the oxygen atom and the NO diatom. As a result of which, the NO₂ molecule excited close to its dissociation threshold behaves as a molecular complex NO-O. The 3-D vibrational density is mainly the one of a 2-D orbiting system, the NO stretch being almost frozen. We present various theoretical approaches and discuss them in connection with experimental data. Finally we want to stress that the long range interactions exist in any triatomic molecule. The question is open to know their consequences on unimolecular reaction processes, such as dissociation.

ROTATIONAL SPECTRA, HYPERFINE STRUCTURE, AND
NUCLEAR MAGNETIC SHIELDING TENSORS
OF $^{33}\text{SO}_2$ AND SO^{17}O

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Precise frequencies for the $1_{11} - 2_{02}$ transition of $^{33}\text{SO}_2$ and SO^{17}O in natural isotopic abundance have been obtained by microwave Fourier transform spectroscopy to yield improved hyperfine constants. Nuclear spin-rotation coupling constants have been determined for $^{33}\text{SO}_2$ for the first time. The same transition was also recorded for $^{32}\text{SO}_2$, $^{34}\text{SO}_2$, SO^{18}O , and vibrationally excited ($v_2 = 1$) $^{32}\text{SO}_2$, in part to allow for a comparison with previously published precise data.

SO_2 is an important interstellar molecule. Continuing our investigations of the rotational spectra of isotopomers of SO_2 ,^{a,b} selected SO^{17}O transitions have been studied in the submillimeter wave region in order to improve and newly determine rotational and centrifugal distortion constants. At present, these measurements cover 540 – 840 GHz with J and K_a up to 63 and 16, respectively. For $^{33}\text{SO}_2$, some transitions with large hyperfine splitting were recorded in the millimeter wave region.

The spin-rotation constants have been used to derive nuclear magnetic shielding parameters which were compared with NMR shifts, data from quantum chemical calculations, and results for the isoelectronic O_3 molecule.

^aE. Klisch, P. Schilke, S. P. Belov, and G. Winnewisser, *J. Mol. Spectrosc.* **186** (1997) 314.

^bS. P. Belov, M. Y. Tretyakov, I. N. Kozin, E. Klisch, G. Winnewisser, W. J. Lafferty, and J.-M. Flaud, *J. Mol. Spectrosc.* **191** (1998) 17.

ANALYTIC METHOD AND SOFTWARE FOR ONE-DIMENSIONAL QUANTUM-MECHANICAL CALCULATIONS

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An extended concept of the Morse oscillator is presented, where the potential is constructed from several smoothly joined Morse-type (ordinary, reversed or pseudo-Morse) components. The elaborated method can be applied to simple quantum systems, such as diatomic molecules, which often can be well approximated as modified Morse oscillators. The analytic procedures of calculating the complete spectrum of the bound and quasi-bound states are described, and the correction method for normalizing the continuum wavefunctions is suggested, which takes account of the rigorous sum rules for the complete set of the energy eigenfunctions ^a. The resulting correction function for the continuum wavefunctions of a diatomic molecule is well described by the Fano line shape function ^b, which is an indication of the partially quasi-discrete nature of the continuous energy spectrum of a diatomic molecule near its dissociation limit.

Making use of exactly solvable model potentials one can perform flexible fit with the available experimental data. As demonstrated elsewhere ^c, this might be helpful in ascertaining the real interaction potentials for simple quantum systems. All the analytic procedures are illustrated on Xe_2 molecule in its 0_g^+ and 0_u^+ electronic states. Based on the method described, the author has composed an easy-to-use Windows 95/98 application for performing high-precision quantum-mechanical computations. It is designed within the Windows development environment Microsoft Visual Basic 6, but all calculations are performed with the help of special 32-bit low-level software. This computational tool is also briefly described in this report.

Research has been supported by Estonian Science Foundation Grants No. 2689 and 3455.

^a M. Selg, Exactly Solvable Modified Morse Potentials for Quantum-Mechanical Applications, *Physica Scripta* (accepted for publication).

^b U. Fano, *Phys. Rev.* **124**, 1866-1878 (1961).

^c M. Selg, *Proc. Estonian Acad. Sci. Phys. Math.* **47**, 29-47 (1998).

**GENERAL CONCEPTS OF THE 1999 VERSION OF THE
HILRAPSS99-HIGH/LOW RESOLUTION
ANALYSIS/PREDICTION OF SPECTRA SOFTWARE**

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The dramatic increase of the computer power during the last years and the integration of symbolic calculation platforms as Mathematica with a powerful user interface makes possible the writing of "stand alone" computer programs doing combined symbolic and numerical calculations.

HILRAPSS99 is an integrated high resolution spectroscopic software running under the Mathematica ver. 3.0 with a powerful user interface allowing the presentation/user input of the physical symbols, parameters and calculation formulae in a quality which we are used by \TeX documents. These symbols and formulae are converted at the same time to executable functions and used for the calculations; also they can be saved in a file and reloaded at any time in the program. The database set up for a molecule contains not only the numerical values of the quantum numbers and parameters, BUT all symbol definitions, matrix elements and formulae.

HILRAPSS99 will allow to do the complete analysis of any type of spectra from the first step of calculating the peak positions and peak intensities from the raw spectrum up to the creation of publication ready tables and figures of the analysed spectra.

This poster will explain the principles and the basic tasks of the HILRAPSS computer program.

- 1) Extraction of spectroscopic data from the raw spectrum for any type of spectra.
- 2) The collection of any spectroscopic data for a molecule in a single "spectrum", appending and merging the different spectra (measured even with different spectroscopic techniques) and the peaklists in a single spectrum.
- 3) Setup of molecule specific database for any kind of molecule, for any kind of energy level structure and any kind of transition type.
- 4) Setup of the theoretical background (formel, matrix elements, group theory calculations etc...) of the molecule under study and the storage of this setup into the database.
- 5) Analysis/Prediction of the spectra using the theoretical background stored in the database. This includes a powerful complete automatic assignment functions of the spectra under analysis.

6) Creation of publication ready tables and figures from the data stored in the database.

Some of the HILRAPSS packages are already finished and tested, a preview of the finished packages will be shown for interested spectroscopists at the conference.

Invited Lectures K

Thursday, September 9, 9:00

Chairman : J.-M. FLAUD

HIGH-RESOLUTION LABORATORY SPECTROSCOPY FOR REMOTE-SENSING OF ATMOSPHERIC TRACE GASES

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Remote-sensing by spectroscopic techniques is a powerful tool for monitoring of the Earth's atmosphere. In the last decades, several advanced space-borne spectrometers have provided a wealth of information about the atmosphere, in many cases also with global coverage. Some instruments are prototypes for a new generation of sensors which will routinely perform measurements from meteorological satellites (such as the European METOP programme). For these and for many other ground-based and air-borne remote-sensing experiments, accurate laboratory reference data (line positions, line intensities, lower states' energies, pressure broadening and shift coefficients, or temperature-dependent absorption cross-sections) are essential.

In this talk, recent laboratory studies in the UV-visible will be reported, with particular focus on applications for the GOME (Global Ozone Monitoring Experiment, in orbit onboard ERS-2 since 1995)^a and SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography, launch in 2000 onboard ENVISAT-1)^b satellite spectrometers. GOME and SCIAMACHY are multichannel diode-array spectrometers covering the 230–790 nm and 215–2385 nm regions, respectively. Both instruments measure sunlight which is backscattered from the Earth's atmosphere and reflected from clouds or from the Earth's surface. From the broad-band medium-resolution spectra recorded with GOME and SCIAMACHY, global concentrations of O₃, NO₂, OClO, BrO, H₂CO, SO₂, and H₂O can be determined. SCIAMACHY will also measure global CO, N₂O, and CH₄ concentrations using dedicated channels in the near infrared (1.9–2.0 μm and 2.2–2.4 μm).

As part of the GOME and SCIAMACHY projects, new measurements of temperature-dependent UV-visible absorption cross-sections of O₃, NO₂, OClO, and BrO were performed in our laboratory using a Bruker IFS-120 HR Fourier-transform spectrometer. In addition, laboratory measurements of temperature-dependent molecular absorption spectra were made with the GOME and SCIAMACHY flight models prior to launch in 1994 and 1998, respectively. The new measurements contribute to improving the existing remote-sensing reference database in the UV-visible spectral region.

^aJ. P. Burrows et al., "The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results", *J. Atm. Sci.* **56**, 151–175 (1999)

^bH. Bovensmann et al., "SCIAMACHY: Mission Objectives and Measurement Modes", *J. Atm. Sci.* **56**, 127–150 (1999)

ELECTRONIC SPECTRA OF CARBON CHAINS IN THE GAS PHASE AND THEIR RELATION TO THE DIFFUSE INTERSTELLAR BANDS

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The electronic spectra of neutral carbon chains, their anions and cations are being observed in the gas-phase. Three different approaches are used. The transitions of the chain radicals, C_nH $n=6,8,10,12$ have been detected by cavity ringdown spectroscopy in a slit discharge. The electronic transitions of the polyacetylene cations, like HC_6H^+ and its cyanoderivative HC_4CN^+ , have been measured at high resolution in cell and jet discharges using frequency modulation absorption spectroscopy. Carbon chain anions of the type C_n^- and C_nH^- have been studied by a two colour resonant photodetachment approach. The case of C_7^- is striking; the origin band of the $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition, as well as the strong vibronic transitions, coincide with diffuse interstellar band absorptions. This provides compelling evidence for the first identification of a carrier.

Poster Session L
Thursday, September 9, 11:00

**IN SITU MONITORING OF STRATOSPHERIC CH₄ AND H₂O
USING TELECOMMUNICATION DIODE LASERS**

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SDLA is a balloon-borne spectrometer devoted to the in situ monitoring of CH₄ and H₂O in the upper troposphere and lower stratosphere using commercial DFB InGaAs laser diodes in combination with differential absorption spectroscopy. Absorption spectra of CH₄ (in the 1.653 μm region) and H₂O (in the 1.393 μm region) are simultaneously sampled every one second by coupling two near-infrared laser diodes to an Herriott multipass cell open to the atmosphere, using optical fibers. The SDLA project started in 1997, supported by the french Spatial Agency (CNES) and the CNRS. To prepare the scientific flights, SDLA has been test-flown in October 98. It has been followed by two flights in the early 99, in the frame of the Third European Stratospheric Experiment on Ozone. Spectra of methane ($2\nu_3$, R(3)) and water vapor ($\nu_1+\nu_3$, P(3)) in the 1 km - 31 km altitude range recorded during these balloon flights will be presented. The balloon-borne diode laser spectrometer will be described and interest for atmospheric sensing of telecommunication DFB InGaAs laser diodes will be discussed.

TEMPERATURE DEPENDENT REFERENCE SPECTRA OF
O₃, NO₂, AND OTHER ATMOSPHERIC TRACE GASES
MEASURED WITH THE SCIAMACHY SATELLITE
SPECTROMETER

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The SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric CHartography) PFM satellite spectrometer is a very sensitive, multichannel grating spectrometer which simultaneously measures in the ultraviolet, visible and near infrared spectral range (235–2385 nm) at a resolution of 0.22–1.5 nm. During the PI- and Delta-PI-period CATGAS (Calibration Apparatus for Trace GAs Spectra), a transportable laboratory set-up for absorption spectroscopy, was connected to the spectrometer by a glass fibre bundle. Absorption spectra of the following atmospheric trace gases were recorded at different temperatures and appropriate partial pressures: O₃ (203–293 K), NO₂ (203–293 K), SO₂ (203–293 K), OClO (293 K), NO (293 K), O₂ (203–293 K), BrO (203–298 K), H₂CO (293 K), H₂O (293 K), CO (293 K), N₂O (293 K), CH₄ (203–293 K), and CO₂ (293 K).

The measured spectra were carefully checked concerning baseline stability and a good signal-noise-ratio, then corrected for straylight, wavelength-calibrated with FTS-spectra recorded previously, and scaled to absolute cross-sections with literature spectra. This data set will be used for the retrieval of atmospheric gas trace gas concentrations and their vertical distributions from the satellite data. Because of the broad wavelength coverage and the large temperature range the data set also provides accurate information for molecular *ab-initio* calculations. It is interesting to note that we have simultaneously measured the absorption of O₃ in the UV-Vis and in the NIR around 1.95–2.04 nm and 2.26–2.39 nm, where accurate line parameters of ozone absorption are available by high-resolution Fourier transform spectroscopy [1–5].

[1] A. Barbe and A. Chichery, *J. Mol. Spectrosc.* **192**, 102–110 (1998)

[2] A. Barbe, J. J. Plateaux, Vl. G. Tyuterev and S. Mikhailenko, *J. Quant. Spectrosc. Radiat. Transfer* **59**, 185–194 (1998)

[3] J. M. Flaud, A. Barbe, C. Camy-Peyret, and J. J. Plateaux, *J. Mol. Spectrosc.* **177**, 34–39 (1996)

[4] A. Barbe, O. Sulakshina, J. J. Plateaux, Vl. G. Tyuterev and S. Bouazza, *J. Mol. Spectrosc.* **175**, 296–302 (1996)

[5] A. Barbe, S. Bouazza, J. J. Plateaux, and M. Jacon, *J. Mol. Spectrosc.* **162**, 335–341 (1993)

REMOTE-SENSING OF ATMOSPHERIC TRACE GASES BY MEANS OF GROUND-BASED HIGH-RESOLUTION SPECTROSCOPY

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Ground-based atmospheric spectroscopy is an important means for the investigation of the Earth's atmosphere. It allows the determination of vertical profiles or column densities of many atmospheric trace gases.

In this work we present solar occultation spectra, i. e. spectra of sunlight transmitted through the atmosphere and collected with the help of a sun tracker. The measurements presented here were performed with different spectrometers:

In Bremen atmospheric spectra are recorded on a regular basis. Sunlight is collected by a suntracker on the roof of the laboratory building and analysed with a Bruker IFS-120 HR Fourier-Transform spectrometer. Measurements are performed in several spectral regions from the UV to the mid-IR with different spectrometer setups. The vertical column densities of atmospheric trace gases (like O₃, NO₂, H₂O, CO₂, CO, CH₄, N₂O, ...) are retrieved in appropriate spectral microwindows.

We also had the chance to perform ground-based atmospheric measurements with the SCIAMACHY satellite spectrometer (235-2385 nm), which will be launched onboard ENVISAT-1. This data set, consisting of solar occultation and zenith sky spectra, not only shows the good quality of the instrument but also helps to test the retrieval algorithms with 'realistic' spectra long before the first spectra from space are at hand

TRACE GAS DETECTION WITH SEMICONDUCTOR LASERS

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Following important developments in semiconductor lasers it is now possible to make high precision measurements of atmospheric trace gas constituents under a wide range of operating conditions. A near infrared TDLAS has been developed ^a to measure methane (CH_4 , $1.65\mu m$) during balloon flights from ground level up to 30 km with 5 metres vertical resolution and sub 10 ppb precision. Such measurements help determine if observed ozone (O_3) loss is caused by air transportation or chemical processing. Future developments of the instrument include fast eddy flux correlation measurements, a multi-species version, open path intercomparison measurements with FTS at landfill sites and the use of new sources covering the atmospheric windows that are located in the mid infrared region.

One such source showing promise, the Quantum Cascade Laser (*QCL*), is currently being characterised at the University of Strathclyde. These devices were first developed and operation demonstrated by Faist et al. in 1994 ^b. Their design allows room temperature operation in the range 3 to 11 μm ^{c,d} and output power up to 300 mW ^e. Sensitive absorption spectroscopy using room temperature QCL was reported in 1998 ^{f,g} and photoacoustic spec-

^aI. F. Howieson, Near-Infrared Tunable Diode Laser Absorption Spectrometer for Trace Gas Detection, PhD Thesis, Department of Physics and Applied Physics, University of Strathclyde, submitted August 1997.

^bJ. Faist, F. Capasso, D. L. Sivco, C. Sirtori, A. L. Hutchinson, and A. Y. Cho, *Science* **264**, 553 (1994).

^cJ. Faist, F. Capasso, C. Sirtori, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, S. G. Chu, and A. Y. Cho, *Appl. Phys. Lett.* **68**, 3680 (1996).

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^eC. Sirtori, Private Communication, ASSET (Intensive Programme in Advanced Semiconductor Science Engineering and Technology), Gas-sensing meeting, Imperial College London (15/04/1999).

^fK. Nanjou, S. Cai, E. A. Wittaker, J. Faist, C. Gmalch, F. Capasso, D. L. Sivco, and A. Y. Cho, *Opt. Lett.* **23**, 219 (1998).

^gS. W. Sharpe, J. F. Kelly, J. S. Hartman, C. Gmalch, F. Capasso, D. L. Sivco, J. N. Bail-

troscopy in 1999^h. Soon high resolution spectroscopy could see further developments regarding field experiments using QCLs.

largeon, and A. Y. Cho, *Opt. Lett.* **23**, 1396 (1998).

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**FTIR REMOTE SENSING OF ATMOSPHERIC COMPOUNDS :
APPLICATION TO GLOBAL CHANGE**

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In this contribution I first underline the need and relevance of measuring gas-phase atmospheric compounds. This point will be illustrated in the context of outstanding environmental issues of current concern such as the greenhouse effect, the ozone-hole in antartica, the increasing levels of UV radiation at ground level and urban air pollution.

I then describe an application of Fourier Transform Infrared Spectroscopy to the monitoring of atmospheric compounds, namely, Solar Absorption Spectroscopy. I first present an overview of the technique and discuss its use as a tool to determine atmospheric composition. I then report FTIR solar spectroscopy measurements carried out at ground level at NCAR employing a spectrometer of 0.06 cm^{-1} resolution. Sample atmospheric spectra and fitting examples are presented for key species relevant to stratospheric chemistry and global change: ozone (O_3), a chlorofluorocarbon (CF_2Cl_2), a greenhouse gas (N_2O), HCl, NO and HNO_3 .

Solar spectroscopy measurements carried out on a regular basis provide long-term trends of key species relevant to global change, e.g., the increase in greenhouse gases and CFC's or the decrease in stratospheric ozone.

THE $4^1\Pi$ AND $5^1\Pi$ STATES OF NaK: THE EXPERIMENTAL AND THEORETICAL STUDY

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The NaK molecule has been the object of intense experimental and theoretical interest, as a prototype of simple heteronuclear system for which both spectroscopic measurements and quantum mechanical calculations are feasible. Recently we have reported experimental investigation^a of two highly excited states of NaK, $3^1\Pi$ and $6^1\Sigma^+$, as well as theoretical study^b of numerous electronic states of this molecule. In this contribution^c we present the first experimental observation of the $4^1\Pi$ and $5^1\Pi$ states of NaK, which correlate with the atom pairs $\text{Na}(3^2S_{1/2}) + \text{K}(5^2P_{3/2})$ and $\text{Na}(3^2S_{1/2}) + \text{K}(4^2D_{5/2})$, respectively. The analysis of two band systems, $4^1\Pi \leftarrow X^1\Sigma^+$ and $5^1\Pi \leftarrow X^1\Sigma^+$, enables accurate molecular constants and RKR potential curves to be determined from the experimental data. The resulting interatomic potentials are compared with the theoretical curves. Additionally, we calculate the R-dependent transition dipole moments for the $4^1\Pi - X^1\Sigma^+$ and $5^1\Pi - X^1\Sigma^+$ transitions^d.

^a A. Pashov, I. Jackowska, W. Jastrzębski, P. Kowalczyk, *Phys. Rev. A* **58**, 1048-1054 (1998).

^b S. Magnier, Ph. Millié, *Phys. Rev. A* **54**, 204-218 (1996).

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^d Research partially sponsored by the KBN grant No. 2 P03B 067 16 and the joint French-Polish "POLONIUM" programme.

THE ROTATIONAL SPECTRA OF IO AND BrO

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IO^a and BrO^b were among the first highly reactive free radicals to be studied by microwave spectroscopy. Although there have been subsequent investigations of the spectra of both molecules, high resolution data for the upper vibrational states ($v > 2$) of the $X_1^2\Pi_{3/2}$ states have remained sparse. The only high resolution work on the $X_2^2\Pi_{1/2}$ state of either molecule is the X_1 - X_2 LMR study of McKellar.^c Because of their possible role in processes affecting upper atmospheric chemistry, we have re-examined the rotational spectra of these molecules under conditions which populate the more highly excited states.

The rotational spectra of IO in vibrational states up to $v = 13$ in the $X_1^2\Pi_{3/2}$ state and up to $v = 9$ in the $X_2^2\Pi_{1/2}$ state have been observed in an O₂ DC discharge over molecular I₂. In addition, I¹⁸O has been observed for both the X_1 and X_2 states up to $v = 5$. This provides the first rotational data for the X_2 state and for I¹⁸O. All data have been analyzed simultaneously with fixed isotopic ratios among the constants. Vibrationally hot BrO has also been observed in an O₂ DC discharge which contains a small amount of Br₂. The BrO measurements are still in progress and have been extended to $v = 6$ for the $X_1^2\Pi_{3/2}$ state and to $v = 3$ for the $X_2^2\Pi_{1/2}$ state of the ¹⁶O species. Br¹⁸O spectra for the vibrational ground state of both the X_1 and X_2 states as well as $v = 1$ of the X_1 state are included in a simultaneous fit of all four isotopomers. Extensive sets of parameters have been derived for both IO and BrO. These will be interpreted in terms of the electronic structure and the interatomic potential and compared with those of related molecules.

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VIBRATIONALLY EXCITED HCN, HC₃N, AND HC₅N TOWARD CRL 618

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Vibrationally excited HC₅N in its $v_{11} = 1$ and $v_{10} = 1$ states has been detected towards the proto-planetary nebula CRL 618 for the first time in interstellar space. We detected relevant vibrational satellites appendant to the transitions $J = 32 - 31$ at 85.2 GHz, $J = 41 - 40$ at 109.2 GHz (Fig. 1) and $J = 51 - 50$ at 135.8 GHz using the IRAM 30 m telescope on Pico Veleta (Sierra Nevada, Spain). Simultaneously, a multitude of vibrationally excited states of HC₃N has been observed ranging from 350 to 1630 K above ground.

Moreover, we detected two absorption features at 29585 MHz and 34954 MHz respectively, which represent the $J = 11, 12$ direct ℓ -type transitions of HCN in its $v_2 = 1$ state. These observations were performed using the Effelsberg 100 m telescope (Germany) and stand for the first detection of its kind. Most of the observed lines show P Cygni profiles indicating that the lines result from a hot, expanding circumstellar envelope close to the exciting star.

Vibrationally excited HC₃N and HC₅N in CRL618

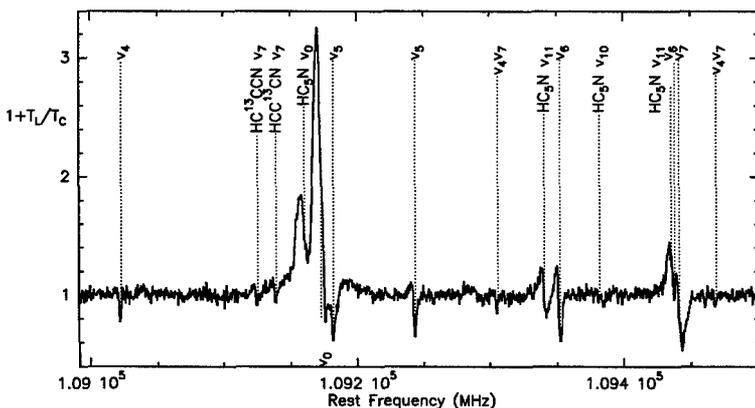


Figure 1: IRAM 30 m spectrum of HC₃N and HC₅N in CRL 618. Vibrationally excited states are marked with dotted lines.

THE ROTATIONAL SPECTRUM OF SO₂F₂. THE FIRST DETERMINATION OF ALL SIX QUARTIC CENTRIFUGAL DISTORTION CONSTANTS FROM THE SPECTRA OF AN ASYMMETRIC ROTOR

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The rotational spectrum of the near-spherical top molecule SO₂F₂ (sulfuryl fluoride) has been investigated by Microwave-Fourier transform spectroscopy and by millimeterwave spectroscopy.

The ground state spectrum has been measured from 10 GHz to 500 GHz. One of the reasons why we were interested in this molecule is that it is nearly-spherical top and we wanted to verify our theoretical prediction that for such a molecule all six quartic centrifugal distortion constants (and nine sextic distortion constants) should be determinable, while for a standard asymmetric rotor Watson^a has shown that only five quartic and seven sextic distortion constants are determinable. The analysis of the spectra confirmed our predictions, because all six quartic constants were well determinable. Because the molecule is relatively heavy, contributions of some sextic constants are too small and we have not been able to determine all nine sextic constants predicted by theory.

The rotational spectra of several vibrationally excited states have been also measured up to 240 GHz.

The microwave spectra of the ³⁴S and ¹⁸O isotopic species have been assigned and a new structure has been determined experimentally and calculated *ab initio*.

^aJ. K. G. Watson *Vibrational Spectra and Structure* (J. Durig, Ed.), Vol.6, pp. 1-89, Elsevier, Amsterdam, 1977.

**PSEUDOROTATION IN 1,3-DITHIOLANE:
A MICROWAVE STUDY**

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The rotational spectrum of the ground, first seven excited states of pseudorotation and the first excited state of the radial mode of 1,3-dithiolane ($C_3H_6S_2$) have been measured in the frequency region 6-72 GHz using conventional microwave Stark modulation spectroscopy as well as waveguide and molecular beam Fourier transform microwave spectrometers. The ground and first pseudorotation excited states have rotational lines of similar intensity for which the effects of a- and c-type Coriolis coupling interaction have been observed in the high-J spectra. From the analysis of these rotation-vibration interaction effects a vibrational energy spacing between these states has been determined to be 185.4522(11) GHz. The most obvious interpretation of this doubling is the existence of a small barrier to pseudorotation through which the molecule interconverts between equivalent ring conformations. Symmetry arguments based on the existence a- and c-type angular momentum operators connecting the coupled vibrational states allow us to conclude that this small barrier occurs at the C_2 twisted configuration and that each of the observed vibrational state consists of a pair of nearly degenerate pseudorotation states due to the existence of highest barriers hindering pseudorotation at the C_s bent ring configurations.

**SUBMILLIMETREWAVE SPECTRUM OF
FLUOROACETYLENE (H–C≡C–F) IN VIBRATIONALLY
EXCITED STATES**

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Recently Dore et al. [1] have extended the measurements of the rotational spectrum of HCCF in the vibrational ground state up to frequency values beyond 1 THz, thus being able to determine a precise value of the sixth order centrifugal distortion constant H_0 . Following this suggestion with the purpose of improving the constants of the excited vibrational states published in [2], we have investigated the submmw-spectra up to 520 GHz. Values of molecular constants – particularly of vibration-rotation interaction constants – are compared with results obtained from the analysis of high resolution IR-spectra [3–5] and results of ab-initio calculations [6].

[1] L. Dore, A. Mazzavillani, L. Cludi, and G. Cazzoli, *J. Mol. Spectrosc.*, **189**, 224-227 (1998).

[2] F. Rohwer, R. Hinze, and A. Guarnieri, *Z. Naturforsch.*, **44a**, 131-138 (1989).

[3] M. Niedenhoff, K. M. T. Yamada, J. Lindenmayer, and H. Jones, *J. Mol. Spectrosc.*, **152**, 213-228 (1992).

[4] A. F. Borro and I. M. Mills, *Chem. Phys.*, **190**, 363-371 (1995).

[5] J. K. Holland, D. A. Newnham, I. M. Mills, and M. Herman, *J. Mol. Spectrosc.*, **151**, 346-368 (1992).

[6] P. Botschwina, M. Oswald, J. Flügge, Ä. Heyl, and R. Oswald, *Chem. Phys. Lett.*, **209**, 117-125 (1993).

HIGH RESOLUTION ANALYSIS OF THE ν_1 AND ν_3 BANDS OF THE $^{17}\text{O}^{17}\text{O}^{16}\text{O}$ AND $^{17}\text{O}^{16}\text{O}^{17}\text{O}$ ISOTOPIC SPECIES OF OZONE IN THE 10 μm REGION

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Using 0.002cm^{-1} Fourier transform absorption spectra of ^{17}O -enriched sample of ozone, an extensive analysis of the ν_3 band together with a partial identification of the ν_1 band of the $^{17}\text{O}^{17}\text{O}^{16}\text{O}$ and $^{17}\text{O}^{16}\text{O}^{17}\text{O}$ isotopic species of ozone has been performed in the 10 μm region. The experimental rotational levels of the (001) and (100) vibrational states could be reproduced using an Hamiltonian matrix which takes into account the expected rovibrational resonances. As for the other C_s -type ozone isotopomers^a, the (001) rotational levels of $^{17}\text{O}^{17}\text{O}^{16}\text{O}$ are involved in both Coriolis and Fermi type resonances with the levels from the (100) vibrational state. On the other hand, for the $^{17}\text{O}^{16}\text{O}^{17}\text{O}$ C_{2v} -type isotopomer, only C-type Coriolis resonances have to be considered. Using an Hamiltonian matrix which takes into account these resonances for the (001)-(100) off-diagonal blocks, and an A-type Watson operator for the diagonal blocks, precise vibrational energies and rotational and coupling constants are deduced.

^aJ.-M.Flaud and R.Bacis, *Spectrochimica Acta*, **A54**, 3 (1998)

HIGH RESOLUTION INFRARED SPECTRUM OF THE RING-PUCKERING BAND, ν_{10} , OF DIBORANE

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We are in the process of studying all the infrared active fundamentals of diborane; the spectrum from 280 cm^{-1} to 2700 cm^{-1} has been recorded, and band-by-band analysis is in progress. The analysis of the lowest frequency band, ν_{10} , centered near 369 cm^{-1} , which results from the ring puckering vibration, will be presented. The spectrum of a sample with boron in natural abundance (19 % ^{10}B , 81% ^{11}B) as well as one enriched in ^{10}B has been obtained with a resolution of 0.0015 cm^{-1} and a S/N of better than 500 to 1. This band appears to be the only unperturbed band in the diborane spectrum, and assignment of not only the fundamental bands but also the hot bands, $2\nu_{10} - \nu_{10}$, of the $^{10}\text{B}_2\text{H}_6$, $^{10}\text{B}^{11}\text{BH}_6$ and $^{11}\text{B}_2\text{H}_6$ isotopomers was straightforward despite the fact that the band centers of all three isotopomers fall within 0.05 cm^{-1} of each other. Band intensities have been obtained for the fundamental bands as well as the hot bands of all three isotopomers. The transition moments μ_b of the hot bands are about 10% lower than would be expected from that obtained from the fundamental bands.

RECENT PROGRESS IN LASER-INDUCED THERMAL ANISOTROPY PATTERNS AND APPLICATIONS

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Optical patterns can be induced by a laser beam, formed in an isotropic absorbing material mounted in a mirrorless experimental set up. The phenomenon is due to laser-induced anisotropy. In fact, a part of the optical power is absorbed by the material which leads to the sample heating: the medium becomes anisotropic due to thermal stress, and the indicatrix of the material becomes an ellipse. The refractive indices of the medium become laser power dependent under strong beam intensity excitation. As a result this refractive index variation modifies the optical properties of the beam and an optical pattern is induced. In the past, this phenomenon has been extensively studied in amplifying media. In most cases, it is a harmful effect : it causes the power losses due to the depolarisation and it is the origin of the beam profile distortion.

Recently this effect has attracted attention again, because in some other type of materials, in appropriate experimental configurations, new spatio-temporal structures have been observed. These new polarisation patterns, that are better understood, present advantages in their applications and render the laser-induced thermal anisotropy effect beneficial.

We review the recent progress in this field. We outline how the potential applications in, for example, a two-dimensional position sensor and actuator and a new type of vectorial stress transducer. Applications on the thermal constants determination and refractive index change measurements are also described.

**ABSOLUTE LINE INTENSITIES
IN THE 2 μm REGION OF $^{14}\text{N}_2^{16}\text{O}$**

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Absorption spectra of N_2O , at room temperature, have been recorded at a resolution of 0.007 cm^{-1} in the range from 4000 to 6000 cm^{-1} using a Bruker IFS120HR spectrometer. Sample pressure/absorption path length products ranging from 7 to $540\text{ hPa}\cdot\text{m}$ have been used. Absolute line intensities have been measured in 19 bands. Using wavefunctions previously determined from a global fit of an effective hamiltonian to about 18000 line positions, parameters of a corresponding effective dipole moment have been fitted to the experimental intensities of cold and hot bands. Results will be presented and discussed.

**ABSOLUTE LINE INTENSITIES MEASUREMENTS IN THE
 $\nu_4 + \nu_5$ BAND OF $^{12}\text{C}_2\text{H}_2$: STUDY OF FORBIDDEN
TRANSITIONS AND HERMAN-WALLIS DEPENDENCIES**

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We have measured absolute line intensities for two bands of $^{12}\text{C}_2\text{H}_2$ near $7.5\mu\text{m}$, namely the $\nu_4 + \nu_5(\Sigma_u^+) - 0(\Sigma_g^+)$ and $\nu_4 + \nu_5(\Delta_u) - 0(\Sigma_g^+)$ bands, using Fourier transform spectroscopy with an accuracy estimated to be better than 2 %. Using theoretical predictions from Watson^a, the observation of the forbidden $\nu_4 + \nu_5(\Delta_u) - 0(\Sigma_g^+)$ band and the Herman-Wallis behaviour exhibited by its rotational lines were shown quantitatively to originate from two types of interactions affecting the levels involved by the bands: l -type resonance and Coriolis interaction. In the case of the $\nu_4 + \nu_5(\Sigma_u^+) - 0(\Sigma_g^+)$ band, the influence of l -type resonance is also confirmed. We attribute the intensity asymmetry observed between the R and P branches of that latter band to a Coriolis interaction with $l = 1$ levels. We did not observe the $\nu_4 + \nu_5(\Sigma_u^-) - 0(\Sigma_g^+)$ band in agreement with Watson's prediction.

^aJ. K. G. Watson, *J. Mol. Spectrosc.* **188**, 78-84 (1998)

THE HOT BAND OF SILANE BETWEEN 2120 AND 2270 cm^{-1}

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The infrared spectrum of the SiH_4 molecule has been recorded between 2040 and 2320 cm^{-1} with the high-resolution Fourier interferometer of the *Laboratoire de Photophysique Moléculaire (Orsay, France)*. In this region, many lines have already been analysed and assigned to the stretching dyad ν_1/ν_3 of $^{28}\text{SiH}_4$, $^{29}\text{SiH}_4$ and $^{30}\text{SiH}_4$ by B. Lavorel et al.^a, but several lines were found to be unassigned in the present spectrum.

Most of these lines are assigned to the hot band stretching-bending tetrad^b $\nu_1 + \nu_2/\nu_1 + \nu_4/\nu_2 + \nu_3/\nu_3 + \nu_4$ minus the bending dyad^c ν_2/ν_4 . These lines will be used to refine the set of Hamiltonian parameters.

The assignment is made using the formalism in the T_d group for the tetrahedral molecules XY_4 .

^aB. Lavorel, G. Millot, Q.L. Kou, G. Guelachvili, K. Bouzouba, P. Lepage, V.L. G. Tyuterev and G. Pierre, *J. Mol. Spectrosc.* **143**, 35-49 (1990).

^bM. Terki Hassaïne, Ch. Claveau, A. Valentin and G. Pierre, to be published.

^cG. Pierre, A. Valentin and L. Henry, *Can. J. Phys.* **64**, 341-350 (1986).

HIGH-RESOLUTION INFRARED STUDY OF *cis*-1,2-DIFLUOROETHYLENE NEAR 1020 cm^{-1}

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Cis-1,2-difluoroethylene was prepared from 1,2-difluorotetrachloroethane and the gas-phase infrared spectrum was investigated in the ν_4 band region ($\approx 1016 \text{ cm}^{-1}$), at a resolution of about 0.002 cm^{-1} , using a tunable diode laser spectrometer. This molecule is a near prolate asymmetric top ($\kappa = -0.841$) of C_{2v} symmetry and the ν_4 vibration of symmetry species A_1 yields a b-type band.

Valuable information for the analysis of the spectrum is mostly provided from the resolved J fine structure of the $^{P,R}Q_K$ subbranches, which have been identified for several K_a values. The Q-branch data represented the starting point of the analysis and their combination with the ground state constants provided an approximate set of upper state constants which allowed prediction of transitions in the P and R branches. Spectral features characteristic of planar molecules are observed in the P and R branches and are due to the near coincidence of transitions between energy levels which become degenerate in the oblate symmetric top limit. The degeneration effect is more pronounced for lower K_a values and, for example, the pair levels $J_{0,J}/J_{1,J}$ and $J_{1,J-1}/J_{2,J-1}$ become almost degenerate for $J \geq 26$ and 32 , respectively. The rovibrational structure of the band exhibits in different spectral regions numerous irregularities due to interactions with nearby states. The perturbations are mainly caused by a c-type Coriolis interaction with $\nu_5 + \nu_{11}$ (B_1) level and by a Fermi resonance with the $2\nu_7$ vibration (A_1).

A detailed analysis in the P, Q, and R branches led to the identification of more than 2800 lines of ν_4 with $J \leq 60$ and $K_a \leq 18$ and to the determination of the upper state constants. In the absence of asymmetry splitting, only the set of even transitions was considered; inclusion in the fit of the unsplit odd ones did not produce any substantial improvement in the spectroscopic parameters.

Interpretation of the spectra and results from the analysis will be presented

MEASUREMENTS OF OZONE ISOTOPOMER ABUNDANCES
USING HIGH RESOLUTION FOURIER TRANSFORM
FAR INFRARED SPECTROSCOPY

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The distribution of ozone isotopomers in ozone mixtures produced by electric discharge in mixtures of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ was measured by high resolution FT-IR spectroscopy. It was of key importance to assess not only the total amount of isotopomers of a certain mass but also the relative amounts of corresponding asymmetric and symmetric ozone species defined as the ratios R_{50} and R_{52} :

$$R_{50} = \frac{[^{16}\text{O}^{16}\text{O}^{18}\text{O}]}{[^{16}\text{O}^{18}\text{O}^{16}\text{O}]} \quad R_{52} = \frac{[^{16}\text{O}^{18}\text{O}^{18}\text{O}]}{[^{18}\text{O}^{16}\text{O}^{18}\text{O}]}$$

For many purposes R_{50} and R_{52} have been assumed to have the statistical value 2.00^a.

Pure rotational spectra in the far infrared region (30-100 cm^{-1}) were recorded for 3 different ozone mixtures, all at 0.00185 cm^{-1} resolution. All the spectra were corrected for sample emission by the method introduced by Ballard et al.^b. Line strengths for individual lines in a particular spectrum were measured by means of a fitting technique taking into account contributions from all other lines in the spectrum. Theoretical line strengths for all six ozone species containing ^{16}O and ^{18}O were obtained from a quantum number dependent dipole operator^c. The ratios between observed and calculated line strengths were used to determine the abundances of individual isotopomers in a particular ozone mixture.

For the 3 mixtures studied the ratio R_{50} was determined to be 2.00(2), 2.01(2) and 2.10(6) respectively and the ratio R_{52} was determined to be 2.52(3), 2.42(10) and 2.46(3) respectively.

^aJ. M. Flaud and R. Basics *Spectrochim. Acta A* **54** 35-63 (1998)

^bJ. Ballard, J. J. Remedios and H. K. Roscoe *JQSRT* **48** 733-741 (1992)

^cL. K. Christensen, N. W. Larsen, F. M. Nicolaisen, T. Pedersen, G. O. Sørensen and H. Egsgaard *J. Mol. Spectrosc.* **175** 220-233 (1996)

**AIR-BROADENING AND SELF-BROADENING OF PURE
ROTATIONAL O₃ LINES
AND THEIR TEMPERATURE DEPENDENCE**

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High resolution FT-IR spectroscopy has been used to obtain highly accurate values of air-broadening and self-broadening coefficients for 107 pure rotational ozone lines and their temperature dependence. Knowledge of such high accuracy pressure broadening coefficients for ozone/air mixtures is important for atmospheric remote sensing studies.

Although many data are already available, much remains to be done with regard to the data and accuracy required for practical applications^a. In many cases the overall uncertainty in the results is estimated only from the spectral noise neglecting errors from other sources. However, with the high signal to noise ratio of modern instruments these have become increasingly important. For example the errors from the apparatus function of the spectrometer, from badly accounted-for contributions of weak and neighboring spectral lines, from thermal sample emission, on the partial pressure of ozone, etc.

Pure rotational spectra in the far infrared region (30 – 100 cm⁻¹) were recorded for 6 different ozone/air mixtures at room temperature and for 2 different ozone/air mixtures at 210 K, all at 0.004 cm⁻¹ resolution. The partial pressures in each particular experiment were chosen to minimize instrumental effects on the final line shapes in the spectrum. Optical path lengths between 17 and 184 cm were used in order to obtain optimal transmittance. Accurate path lengths were calculated from the recorded interferograms. Furthermore the spectra were corrected for sample emission by the method introduced by Ballard et al^b. Line strengths and line widths for individual lines in each particular spectrum were measured by means of a fitting technique that includes the contributions from all other lines in the spectrum. The partial pressure of ozone and the temperature of each sample were calculated from the observed line strengths with reference to the theoretical line strengths obtained from a

^aR.R.Gamache, E.Arié, C.Boursier and J-M. Hartmann *Spectrochim.Acta A* **54** 35-63 (1998)

^bJ.Ballard, J.J.Remedios and H.K.Roscoe *JQSRT* **48** 733-741 (1992)

quantum number dependent dipole moment operator^c.

In estimating the overall uncertainty in the pressure broadening coefficients we have thus taken into account several important theoretical and experimental errors that are usually ignored.

^cL.K.Christensen,N.W.Larsen,F.M.Nicolaisen,
H.Engsgaard *J.Mol.Spectrosc.* **175** 220-233 (1996)

T.Pedersen,G.O.Sørensen and

**THE IMPORTANCE OF NO+O COLLISIONAL
RELAXATION TO THERMOSPHERIC COOLING
AND REMOTE SENSING OF NO**

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Nitric oxide is an important trace constituent throughout the atmosphere. In the stratosphere, the NO involved odd nitrogen chemistry controls the O₃ abundance. Moreover, thermospheric NO plays a key role in thermospheric cooling due to its 5.3 μm emission affecting the radiative budget of the upper atmosphere. The characterization of the radiative properties of thermospheric NO is important for the quantification of thermospheric cooling. On the other hand, the remote sensing of stratospheric NO by means of space borne limb radiance measurements requires an accurate model of NO thermospheric absorption and emission, which affect stratospheric radiances measured outside the atmosphere. The assumption of local thermodynamic equilibrium (LTE) does not hold for thermospheric NO vibrational, rotational, and spin orbit states. Thus, non-LTE state distributions must be modeled in order to constrain the radiative properties of thermospheric NO. The most important process affecting the NO state distribution is the collisional quenching and excitation by NO+O. Vibrational NO+O quenching rates have been determined by different laboratory measurements showing high deviations from each other. Rotational and spin relaxation rates have only been measured for other collisional systems (i.e. NO-Ar, NO-He, etc.). This paper aims to demonstrate the necessity of further laboratory measurements of vibrational, rotational, and spin NO+O relaxation rates. In this sense, the sensitivity of thermospheric cooling to NO+O collisional relaxation rates will be demonstrated by non-LTE model calculations. The accuracy limitation of the inversion of stratospheric NO from space borne limb radiance measurements due to unconstrained NO+O relaxation rates has been assessed in retrieval simulations.

PRECISE MEASUREMENT OF TEMPERATURE DEPENDENT PRESSURE EFFECTS

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High resolution data of pressure effects are important for modeling planetary atmospheres and for astrophysical observations^a. Pressure effects are caused by molecular interaction which depend on the particle density and the relative velocity of the collision partners.

An efficient cooling system for a multipass absorption cell with an absorption length of about 134 m (144 passes) is presented. With this cooling system, which also allows heating, the temperature interval between 110 K and 340 K can be covered.

With the presented setup a temperature stability better than 1 K over two hours and a homogeneous temperature distribution along the cell can be achieved.

Measurements on CO₂ with H₂ are in progress and will be presented.

^aG. Winnewisser, T. Drascher, T. Giesen, I. Pak, F. Schmùlling, R. Schieder, *The tunable diode laser: a versatile spectroscopic tool*, Spectrochim. Acta, in press

COLLISION LINE NARROWING AND MIXING FOR H_2O DOUBLETS NEARBY 2000 cm^{-1}

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Two resolved and five unresolved H_2O doublets near 2000 cm^{-1} broadened by N_2 and Ar have been recorded with the Fourier transform spectrometer of Paris VI University with a spectral resolution of 0.005 cm^{-1} . The data processing takes into account the spectrometer apparatus function both collision narrowing and line mixing. The apparatus function was determined on the basis of solution of the Fredholm equation of the second kind performed with the help of discrete Fourier transformation, using low pressure CO reference lines recorded simultaneously with H_2O ones.. The line intensities, N_2 and Ar pressure broadening and line shifting coefficients, line narrowing and line mixing parameters were determined. It was found that line mixing plays less significant role than line narrowing for all the considered doublets. The authors from Tomsk acknowledge the support by Russian Foundation for Fundamental Research (Grants 98-02-17772, 98-02-16375). This study has been performed in the framework of agreement between CNRS and Russian Academy of Science.

N_2 BROADENING IN R BRANCH OF THE (010)-(000) BAND OF H_2O

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H_2O lines of (010)-(000) band broadened by N_2 were studied in the 1850-2200 cm^{-1} region with a FT spectrometer apparatus function close to the Doppler line shape. It has been possible to determine this apparatus function with an accuracy high enough to analyse the pressure broadened absorption line profiles and to evidence the deviations from the Voigt profile.

The measurements were made with the Fourier transform spectrometer of Paris VI University for different pressures of the gas mixture ($P(H_2O)=0.366-12$ Torr and $P(N_2)=0-400$ Torr).

The line half-width determinations were made by nonlinear least-squares fitting of a calculated line, described by the Rautian-Sobelman profile, to the measured ones. The N_2 -broadening coefficients have been deduced for the different gas pressures. The narrowing parameter has been determined for some lines. Calculations of N_2 -induced linewidth coefficients were performed using Anderson-Tsao-Curnutte theory considering dipole-quadrupole, quadrupole-quadrupole, induction and dispersive interactions.

The authors from Tomsk acknowledge the support by Russian Foundation for Fundamental Research (Grants N 98- 02-16375, N 98-02-17772). This study has been performed in the framework of agreement between CNRS and Russian Academy of Science.

THE HIGH RESOLUTION INFRARED SPECTRUM OF DIMETHYLETHER

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Although the microwave spectrum of dimethylether is now fairly well known,^a almost no investigations have been carried out under high resolution on its infrared spectrum. This is primarily due to the fact that dimethyl ether is a somewhat heavy molecule displaying a very congested infrared spectrum. In addition to that, the nonrigidity of dimethylether, due to the two internally rotating methyl groups, also leads to an intricated spectrum as the first torsional states corresponding to the two large amplitude internal rotation modes are usually populated at room temperature.

The Fourier transform spectrometer coupled to a supersonic slit jet system in Brussels and the diode laser spectrometer, also coupled to a slit jet system, in Orsay have been used to record the infrared spectra of several fundamental bands of dimethylether. The low rotational temperature achieved with both apparatus, about 20 K, allowed us to greatly simplify the spectra and made it possible to carry out the assignment of several bands. The *b*-type ν_6 band, around 933 cm^{-1} , and the *a*-type ν_{17} and ν_{21} bands, around 2817 and 1103 cm^{-1} , respectively, could be assigned up to $J \sim 20$. These bands were then fitted to a Watson-type Hamiltonian written with the *A* reduction. No obvious perturbation effects could be detected and the wavenumbers could be reproduced within experimental uncertainty.

Work is still in progress for the *c*-type ν_{20} and ν_{13} bands, around 1170 and 1460 cm^{-1} , respectively. Since for that latter band accurate diode laser measurements are available, we may be able to observe some broadening of the lines due to the large amplitude motions.

^aW. Neustock, A. Guarnieri, J. Demaison, and G. Wlodarczak, *Z. Naturforsch. A*, **45**, 702-706 (1990).

ON ISOTOPE EFFECT IN THE XH_2 - XHD MOLECULES
WITH AN ARBITRARY VALUE OF EQUILIBRIUM
INTERBOND ANGLE

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General results and formulas of the earlier derived “expanded” local mode approach^a and isotopic substitution theory^b were used as the basis for deriving relations which connect harmonic frequencies ω_λ , anharmonic parameters $x_{\lambda\mu}$, rotation- vibration parameters α_λ^β , centrifugal distortion coefficients τ , etc., of a XH_2 molecule and its substituted species XHD for molecules with an arbitrary value of equilibrium interbond angle α_e .

^aO.N. Ulenikov, R.N. Tolchenov, and Q.-S. Zhu, *Spectrochim. Acta*, **A52**, 1829-1841 (1996).

^bA.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov, *J. Mol. Spectrosc.*, **85**, 462-479 (1981).

ROVIBRATIONAL STRUCTURE USING
QUANTUM-CLASSICAL CORRESPONDENCE: HOW
PROMINENT IS THE INFLUENCE OF THE
INTRAMOLECULAR POTENTIAL ON THE QUALITATIVE
FEATURES OF THE SYSTEM OF ENERGY LEVELS ?

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The idea of the work is to describe the qualitative structure of molecular rotational spectra on the basis of the complete vibration-rotation Hamiltonian (known as the Wilson-Howard Hamiltonian) without going to an effective Hamiltonian and to relate such qualitative phenomena as existence and modifications of the cluster and branch structures *directly* to the parameters of the molecular potential (force field constants) and of the rotation-vibration interaction.

As an example we consider a tetrahedral molecule A_4 . We describe the rotational structure of the ground state of this molecule and of the states corresponding to the excitation of its triply degenerate vibrational mode F_2 using several models for the inter-atomic potential (pairwise atom-atom harmonic or Morse potential, standard normal mode harmonic potential, etc).

The basis of the analysis is the well known idea of associating clusters of levels in the rotational energy spectrum with stationary axes of classical rotation. A number of principal stationary axes which form the set of *relative equilibria* of the rotational problem and exist at any angular momentum J are fixed due to symmetry. For these axes, calculations can be made directly using the total vibration-rotation Hamiltonian.

In the simplest situation of the ground vibrational state, we neglect vibrational kinetic energy and simply consider how the molecule distorts its equilibrium configuration (which is tetrahedral at $J = 0$) when rotating around a particular stationary axis [2]. When the vibrational mode is excited we consider vibrational relative equilibria using a polyad approximation and associate these equilibria with stationary axes. Classical energy calculated for these particular kinds of stationary vibration-rotation motion, i.e., for the non-linear normal modes or the basic periodic orbits of the total rotation-vibration system, give points of reference for the description of the cluster and branch structure of the quantum energy spectrum.

Group theory plays an important role in the analysis. The study of the fixed points of the action of the T_d group on the rotational phase space S_2 (a

sphere) and on the reduced vibrational space of the triply degenerate mode in the polyad approximation CP_2 (a complex projective space) is required to find and characterize relative equilibria [1]. The concept of local symmetry group (stabilizer) of the axis (of the equilibrium) is fundamental to the calculation of the centrifugal distortion of the molecular equilibrium configuration.

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**ALTERNATIVE CHOICES OF QUANTUM NUMBERS.
DEFECTS OF LABELING SCHEMES AND CLASSICAL
MONODROMY**

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Interpretation and classification of molecular energy levels and corresponding spectroscopic transitions is traditionally carried out in terms of quantum numbers which have "good" physical meaning for some specific limiting cases of intra-molecular interactions. Classical example is various sets of quantum numbers for different Hund's cases in diatomic molecules.

The aim of the present study is to analyze the qualitative effects associated with the existence of alternative schemes of "good" quantum numbers within a parametric family of problems and to consider the transition between these alternatives which can occur when some control parameters (strict integrals of motion such as energy, total angular momentum, approximate integrals such as polyad quantum numbers, or external field parameters) are varied. The analysis is done using purely quantum, semi-quantum, and purely classical approach.

Purely quantum mechanical computation exhibits the universal phenomenon of the redistribution of energy levels between branches. The semi-quantum analysis (with certain dynamical variables treated as classical and the rest as quantum variables) provides the interpretation of this redistribution in terms of "diaboloic points", that is singularities related to degeneracy of classical energy surfaces corresponding to different quantum states [1]. The completely classical study demonstrates the relation between classical monodromy [2], the absence of global action-angle variables, the presence of point defects in the lattice formed by quantum numbers, and the redistribution phenomenon.

The detailed quantum, semi-quantum and classical study is carried out for the toy model of two coupled angular momenta \mathbf{S} and \mathbf{N} with the Hamilton function [3]

$$H = \frac{1-\gamma}{|\mathbf{S}|} S_z + \frac{\gamma}{|\mathbf{N}||\mathbf{S}|} (\mathbf{N} \cdot \mathbf{S}), \quad 0 \leq \gamma \leq 1, \quad (1)$$

and γ a coupling parameter. We consider this problem as a one-parameter family for arbitrary *fixed* amplitudes $|\mathbf{N}|$ and $|\mathbf{S}|$ of the angular momenta and focus on the case $|\mathbf{N}| > |\mathbf{S}|$. It can be shown that the classical monodromy exists when

$$\frac{|\mathbf{N}|}{2|\mathbf{N}| + |\mathbf{S}| + 2\sqrt{|\mathbf{N}||\mathbf{S}|}} \leq \gamma \leq \frac{|\mathbf{N}|}{2|\mathbf{N}| + |\mathbf{S}| - 2\sqrt{|\mathbf{N}||\mathbf{S}|}}, \quad (2)$$

and in the limit $|S|/|N| \rightarrow 0$ this interval of the values of γ shrinks towards one point $\gamma = 1/2$ which is precisely the value of γ at which the “diabolic point” of the conical intersection of the rotational energy surfaces happens. Several types of physical systems (such as atoms and molecules in Rydberg states under the presence of external fields, vibrationally excited linear molecules, rotationally and vibrationally excited spherical tops, ...) are expected to exhibit this phenomenon. Suggestions for experimental and extensive numerical confirmations of the manifestation of classical monodromy and its generalizations in intermolecular dynamics are presented.

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**HIGH RESOLUTION ELECTRONIC SPECTRA OF CARBON
CHAIN RADICAL CATIONS BY FREQUENCY MODULATION
ABSORPTION SPECTROSCOPY**

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A sensitive and generally applicable technique for direct absorption spectroscopy of electronic transitions of carbon chain radicals in the gas phase is presented. The method is based on a simultaneous frequency modulation of a cw ring laser and production modulation of transients generated either in a liquid-nitrogen cooled hollow cathode discharge or a pulsed supersonic slit jet plasma. The analyses of the achieved rotationally resolved spectra of triacetylene cation and its isotopic derivatives HC_6D^+ and DC_6D^+ are used to discuss the characteristics of the set-up.

**ROTATIONALLY RESOLVED ELECTRONIC ABSORPTION
SPECTRA OF CYANOPOLYACETYLENE CATIONS****WAYNE E. SINCLAIR,****DAVID PFLUGER, HAROLD LINNARTZ, JOHN P. MAIER,***Institute for Physical Chemistry, Klingelbergstrasse 80, CH-4056 Basel,
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The high resolution absorption spectra of the $A^2\Pi \leftarrow X^2\Pi$ electronic origin band transitions of the isoelectronic pair of cations, NC_5H^+ and NC_4N^+ have been obtained. The cations are generated in a liquid-nitrogen cooled hollow cathode discharge incorporated in a White cell and detected using a frequency-discharge double modulation technique. Rotational analyses yields accurate molecular parameters of the cations in the electronic ground and excited state for both spin-orbit components. A detailed characterisation of these compounds by means of their electronic transitions provides important information for the identification of such species as possible carriers of the optical diffuse interstellar bands. A perturbation of the excited state of the dicyanoacetylene cation could be observed. It is induced by the presence of a nearby $B^2\Sigma_g^+$ state, estimated at 240 cm^{-1} above the $A^2\Pi_g$ state.

**SPECTROSCOPIC AND THEORETICAL
CHARACTERIZATION OF LINEAR CENTROSYMMETRIC
 $N \equiv N \cdots H^+ \cdots N \equiv N$**

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The first high resolution infrared spectrum of the ionic complex $N_2 \cdots H^+ \cdots N_2$ and its deuterated derivative is reported. The spectra were obtained in direct absorption in a supersonic slit nozzle plasma. The observed rovibrational transitions were assigned to the ν_3 NN antisymmetric stretching vibration and the spectrum is consistent with a linear centrosymmetric equilibrium structure. The band origin is found at $2352.2364(6) \text{ cm}^{-1}$ and the ground state rotational constant is determined as $B'' = 0.081809(14) \text{ cm}^{-1}$. The assignment is supported by *ab initio* calculations including electron correlation effects. The best estimate for the equilibrium structure is $R_e(\text{NN}) = 1.095 \text{ \AA}$ and $r_e(\text{N} \cdots \text{H}) = 1.277 \text{ \AA}$. The transition moment of the ν_3 band of $N_2 \cdots H^+ \cdots N_2$ is predicted to be 0.21 D, an order of magnitude larger than for the NN stretching vibration of HN_2^+ . The equilibrium dissociation energy D_e for fragmentation into N_2 and HN_2^+ is calculated to be $\sim 5900 \text{ cm}^{-1}$.

AXIAL AND EQUATORIAL HYDROGEN BONDS

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Hydrogen bonding has been the subject of considerable research effort over the years due to its central role in many chemical, physical and biological phenomena. The intrinsic properties of the hydrogen bond can be obtained from the study of isolated hydrogen-bonded dimers in gas phase. In recent years such studies have been undertaken in the collisionless environment of supersonic jets, where complexes are easily formed and can be probed using different spectroscopic methods. An important type of hydrogen bond dimer $B \cdots HX$ (where $X = F, Cl, \text{etc}$) is that in which the proton acceptor B carries two non-equivalent lone electron pairs. These non-equivalent binding sites would give rise in some ring molecules to two different axial and equatorial forms when a hydrogen bond dimer is formed. We recently reported the first experimental observation of axial and equatorial hydrogen-bonded dimers in the heterodimers pentamethylene oxide^a and pentamethylene sulphide^b in a pulsed supersonic expansion. In this communication we present the results on related complexes, which prove that the hydrogen bond constitute a very sensitive test for the detection of non-bonding electron pairs.

^aS. ANTOLÍNEZ, J. C. LÓPEZ AND J. L. ALONSO, *Angew. Chem. Int. Ed. Engl.* (in press).

^bM. E. SANZ, J. C. LÓPEZ AND J. L. ALONSO *Chem. Eur. J.* (in press)

SYSTEMATIC VIBRATIONAL SHIFTS OF CARBON DIOXIDE MONOMERS AND DIMERS TRAPPED IN VARIOUS MATRICES

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The amount and the sign of vibrational shifts in matrix-trapped molecules are known to vary significantly as a function of matrix material, vibrational mode and temperature. Systematic study of vibrational shifts in matrix environment and in the gas phase allows for new insights into the nature of intermolecular interactions. Specifically, this concerns the study of the vibrational origin shifts upon formation of weakly bound van der Waals complexes or dimers. Until recently, however, a wide set of experimental data on vibrational shifts in vdW dimers have never been attempted to systematize.

This work aims at mutual reanalysis of the existing literature Raman and infrared data together with new FTIR spectroscopy data of our own. Carbon dioxide monomers and dimers are the carriers of our chosen spectra. Useful correlations of the shifts with the matrix material properties are established, which can be used in predictions of vibrational origins either in matrices or in the gas phase. Our analysis made it possible in particular to position the yet unknown vibrational origins for $(\text{CO}_2)_2$ bending vibrations in the gas phase at 669.8 cm^{-1} and 665.6 cm^{-1} .

INFRARED SPECTRA OF CO-H₂O AND CO-D₂O CLUSTERS IN Ar MATRIX

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CO-H₂O clusters in Ar matrix exhibit several absorption peaks in the CO stretching region, which should originate in the clusters of the different sizes ^a, i.e., (CO)_n-(H₂O)_m. The interpretation and the assignment for the peaks, however, have not been settled. The difficulties in assignment are caused mainly by the fact that the spectral features depend strongly on the experimental parameters ^b such as sample ratio, deposition rate, deposition temperature, temperature cycle, and impurities. It is important to record the spectra under well controlled condition which guarantees the reproducibility to establish unambiguous assignments.

In the present study, we have measured the spectra with wider choices of experimental parameters than those reported previously. Much attention has been paid to secure the spectral reproducibilities; each measurement has been repeated independently at least twice with the same experimental parameters mentioned above. The infrared spectra of CO-D₂O clusters in Ar matrix were measured for the first time in the present study, and they show very similar features to the spectra of CO-H₂O clusters. The data thus obtained were analyzed considering the relative intensities of the peaks appeared in the CO, OH, and OD stretching regions. The blue shifts of CO stretching band for CO-H₂O and CO-D₂O clusters from the monomer band found in Ar matrix are consistent with those observed in gas phase ^c. The assignment for both CO-H₂O and CO-D₂O clusters will be presented.

^aA. Givan, A. Loewenschuss, and C. J. Nielsen, *J. Chem. Soc., Faraday Trans.* **92**, 4927 (1996).

^bH. Dubost and L. Abouaf-Marguin, *Chem. Phys. Lett.* **17**, 269 (1972)

^cM. D. Brookes and A. R. W. McKellar, *J. Chem. Phys.* **109**, 5823 (1998)

CONSTRUCTING THE PERFECT GROUND STATE POTENTIAL FOR WATER

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The infrared spectrum of water is possibly one of the most well studied and yet portions of it are still poorly understood. Recently, significant advances have been made in assigning water spectra using variational nuclear motion calculations[1]. The major factor determining the accuracy of ro-vibrational spectra of water is the accuracy of the underlying Potential Energy Surface. Even the most accurate *ab initio* Potential Energy Surface [2] does not reproduce the Born-Oppenheimer surface to sufficient accuracy for spectroscopic studies. Furthermore, effects beyond this model such as the relativistic correction [3], adiabatic correction [4] and the non adiabatic correction need to be considered. We will discuss further alterations to *ab initio* calculations by introducing a barrier to the water potential. This barrier attempts to represent the change in potential from linear to equilibrium. We show the improvements this has on calculated energy levels by comparison with the HITRAN database [5]. These results are now leading the way to an improved spectroscopic potential.

[1] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, *Science* 277 (1997) 346.

[2] H. Partridge and D. W. Schwenke, *J. Chem. Phys.* 106 (1997) 4618.

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[5] L. S. Rothman et al, *J Quant. Spectrosc. Radiative Transf.* 48(1992)469

HIGH RESOLUTION MICROWAVE SPECTROSCOPY OF CHIRAL MOLECULES

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The high-resolution microwave spectra of two chiral molecules, butan-2-ol and methyl disulphide, have been recorded in the range 6-18 GHz. Using a semi-rigid asymmetric rotor model, and by comparison with high quality *ab-initio* calculations, three conformations of butan-2-ol have been detected, and their spectra assigned. The spectrum of methyl disulphide, previously observed at low resolution ^a has been re-recorded, and the higher resolution has enabled a study to be made of the effect of internal rotation of the methyl groups. In addition to the above, preliminary work on the van der Waals dimers of the above molecules will be presented.

^aD. Sutter, H. Dreizler and H.D. Rudolph *Z. Naturforschg* **20a** (1965), 1676-1681.

ROTATIONAL ANALYSIS OF THE
 $[O_2(^1\Delta_g)_{v=0}]_2 \leftarrow [O_2(^3\Sigma_g^-)_{v=0}]_2$ **TRANSITION**
OF THE O_2 DIMER NEAR 632.6 nm

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The rotationally resolved absorption spectrum of the $[O_2(^1\Delta_g)_{v=0}]_2 \leftarrow [O_2(^3\Sigma_g^-)_{v=0}]_2$ transition of the O_2 dimer has been recorded near 632.6 nm by continuous wave Cavity Ring Down Spectroscopy and Intracavity Laser Absorption Spectroscopy in a supersonic slit jet expansion of pure O_2 . A quadratic dependence of the absorption in the jet versus the stagnation pressure is observed. A rotational temperature of 12 K is derived from the O_2 dimer analysis. The high spectral resolution of the CW-CRDS measurements, limited by residual Doppler broadening in the jet, and the low temperature allow for the first time a rotational analysis of this open-shell complex. The rotational structure extends from 15800 to 15860 cm^{-1} . The identified rotational transitions correspond to sub-bands of a slightly asymmetric prolate top arising from two types of symmetry (A_1^+ and B_1^-). The analysis of two sub-bands centered at 15808.42(3) [$A_1^+ \leftarrow B_1^-$] and 15813.15(4) cm^{-1} [$B_1^- \leftarrow A_1^+$] gives the effective rotational constants:

$[O_2(^1\Delta_g)]_2 (B' + C')/2 = 0.0638(57)$ for $K' = 1 (A_1^+)$ and $0.0634(29) cm^{-1}$ for $K' = 1 (B_1^-)$

$[O_2(^3\Sigma_g^-)]_2 (B'' + C'')/2 = 0.0966(61)$ for $K'' = 0 (B_1^-)$ and $0.0936(30) cm^{-1}$ for $K'' = 0 (A_1^+)$

close to the calculated *ab initio* values:

$(B' + C')/2 = 0.0602$ for $K' = 1 (A_1^+)$ and $0.0603 cm^{-1}$ for $K' = 1 (B_1^-)$

$(B'' + C'')/2 = 0.0803$ for $K'' = 0 (B_1^-)$ and $0.0856 cm^{-1}$ for $K'' = 0 (A_1^+)$

From the H rectangular geometry of the dimer in the two singlet states, the mean distances between the two monomers are derived and compared to *ab initio* values. A vibrational assignment is given for these two sub-bands and proposed for the whole band.

INVESTIGATION OF QUALITATIVE PHENOMENA IN ROTATIONAL DYNAMICS OF MOLECULES. MICROSCOPIC APPROACH TO THE PROBLEM

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In the standard theory of rovibrational dynamics of molecules, the molecular motion is assumed to be approximately separated into uncoupled rotational and vibrational motions. In this way rovibrational interaction is assumed to be small enough and can be taken into account in terms of the perturbation approach. However, such a treatment is invalid in the case that some of nuclei in molecules execute large amplitude motions or a molecule is excited to high rotational states. In such molecules the rovibrational interaction becomes significant enough to cause qualitative changes in rotational dynamics which can not be described in the context of the usual model.

Our method consists in construction of the effective rotational Hamilton function, which the most part of the rovibrational interaction is involved in. In principle, such a function can be obtained in the context of phenomenological approach, but in this case a theory can not predict critical values of the angular momentum (or some another control parameters) at which qualitative changes of rotational dynamics would appear for a given molecule. Contrastingly, we obtain the effective rotational Hamilton function from the total classical rovibrational Hamiltonian by its minimizing with respect to vibrational coordinates and conjugated momenta. Investigation of the stability of effective rotational Hamilton function's stationary points allows us to reveal qualitative changes of rotational dynamics and to predict the critical values of the angular momentum at which the molecular rotation changes its character qualitatively.

Results of such an approach for water-like molecules (both symmetrical and nonsymmetrical ones) are presented, all internal degrees of freedom being taken into account.

**ROVIBRATIONAL ENERGY TRANSFER IN METHANE
STUDIED BY LASER-INDUCED
FLUORESCENCE AND TIME RESOLVED IR-IR DOUBLE
RESONANCE**

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Rovibrational energy transfer processes occurring in methane upon molecular collisions have been investigated from laser-induced fluorescence measurements and from time resolved IR-IR double resonance measurements. In both cases, CH₄ was excited to the 2ν₃ vibrational state by an optical parametric oscillator (OPO) pumped by a Nd:YAG laser. Hot fluorescence from overtone and combination states was monitored for both infrared active modes: ν₃ near 3.3 μm and ν₄ near 7.5 μm^a. The time evolution of fluorescence intensities was well reproduced from a numerical model based on a simplified kinetic scheme of the relaxation. The double resonance (DR) measurements were performed by using a laser diode as a probe. By scanning the frequency of this laser diode over the range 2938 to 2983 cm⁻¹, we have found numerous DR signals corresponding to unknown rovibrational transitions involving states of the pentade and of the tetradecade, and from these signals we have deduced relaxation times corresponding to various relaxation processes.

^aL. Doyennette, F. Menard-Bourcin, J. Menard, C. Boursier and C. Camy-Peyret
J. Phys. Chem. **102**(3849), 28 May 1998.

**THE HIGH-RESOLUTION INFRARED SPECTRUM OF
1,2,4-TRIAZINE VAPOR BETWEEN 550 AND 1700 cm^{-1}**

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The IR spectrum of gaseous 1,2,4-triazine has been measured with a resolution of ca. 0.003 cm^{-1} between 550 and 1700 cm^{-1} . From a comparison with the liquid phase IR and Raman spectra and using ab initio predictions, most of the fundamental bands of 1,2,4-triazine below 1600 cm^{-1} have been assigned. The rotational structure of twelve of the bands in the gas phase spectra have been analysed via the Watson Hamiltonian model to yield spectroscopic constants. A number of local resonances have been identified and interpreted.

Poster Session M
Thursday, September 9, 20:00

**TIME RESOLVED DOPPLER-LIMITTED FOURIER
TRANSFORM EMISSION SPECTRA OF $^{14}\text{N}_2$**

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N_2 molecule is thoroughly investigated due to its importance mainly in the upper atmosphere, in surface treatments of various materials, in plasma chemistry in general. A characteristic feature of this molecule is the complex energy transfer processes within the first excited states. The desire to explain and quantify these processes have stimulated number of research programs on this molecule. For the $\text{B } ^3\Pi_g$ state, the problem of energy transfer processes of the first vibrational levels strongly coupled to those of the $\text{W } ^3\Delta_u$ state is still open. Our purpose is to investigate the kinetic of these levels by means of Time Resolved Fourier Transform Spectroscopy (TR-FTS) in the early afterglow of a pulsed microwave discharge. Time resolved spectra for this kinetic study will be presented.

NUCLEAR SPIN CONVERSION IN CH₃F INDUCED BY ALTERNATING ELECTRIC FIELD

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New experimental setup developed in Lille allows to study the conversion of nuclear spin isomers of polyatomic molecules. Using this setup we investigated spin isomers of CH₃F molecules. CH₃F has two isomers: ortho (total spin of the three protons equal 3/2) and para (spin 1/2). The conversion of CH₃F spin isomers is governed by the specific mechanism based on the mixing of the ortho and para states by *intramolecular* hyperfine interactions. Recently, this mechanism was confirmed by observing the level-crossing resonances in the conversion of CH₃F molecules subjected to the DC electric field.^c

We present here the new experimental test of the CH₃F conversion mechanism. In our experiment the ¹³CH₃F molecules were subjected to an *alternating* electric field. For the amplitude of the AC electric field below 500 V/cm we observed little change of the conversion rate. If an electric field reaches the value sufficient to cross the ortho and para states of the molecule, sharp 10 times increase in the conversion rate occurs.

A theoretical model for the CH₃F conversion in AC electric field has been developed and compared with the experimental data. We discuss also a few possible applications of the spin isomer conversion induced by AC electric field.

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^bP.L.C. thanks the Region Nord Pas de Calais for his financial support

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NEW SEARCH FOR PARITY VIOLATING EFFECTS IN CHIRAL MOLECULES

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In 1974, Rein [1] suggested that a difference between energy levels of right- and left-handed chiral molecules could be induced by neutral weak interactions. Its experimental manifestation could be a frequency difference between the rovibrational spectra of the enantiomers of a chiral molecule, as proposed by Letokhov [2].

The molecule CHFCIBr was suggested as a good candidate for such an experiment [3]. But in 1976, the resolved enantiomers of this simple chiral molecule were not available and the unique test of parity violation on separated enantiomers has been performed on camphor [4] in 1977 with a sensitivity of a few 10^{-8} , far from theoretical estimates.

Since that time, no similar experiment has been tried for two reasons: the non-availability of the enantiomers and the discouraging smallness of the effect, although its estimate is still today very uncertain. However, a lot of theoretical predictions has been performed, mainly on biomolecules [5] since some authors speculated that the symmetry breaking between right and left species of these molecules could find its origin in the energy difference induced by the weak interaction [6].

We will present the first experimental test of the frequency difference in the spectrum of the enantiomers of a chiral molecule with a sensitivity in the range given by the theoretical predictions [7,8]. This experiment has been performed with CHFCIBr on a hyperfine component of a rovibrational line belonging to the ν_4 band at $9.4\mu\text{m}$. No significant difference has been observed with a relative sensitivity of 4.10^{-13} and we will propose some methods to improve significantly this sensitivity in the future.

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FIRST OBSERVATION OF MATTER WAVE INTERFERENCE ON A K_2 MOLECULAR BEAM

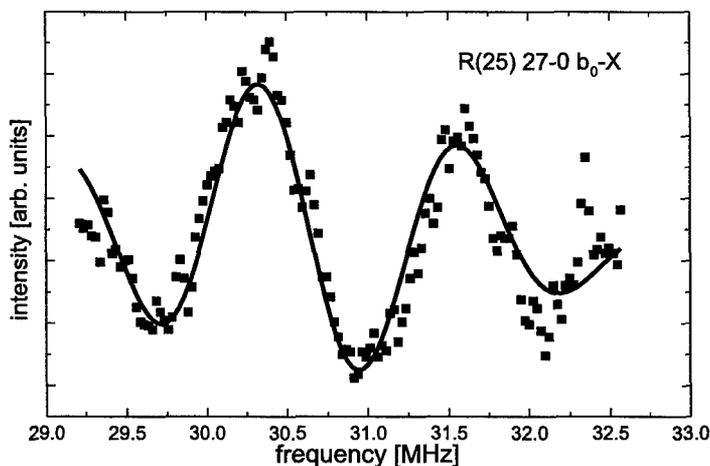
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We will report of the first observations of matter wave interferences (see figure) on a K_2 molecular beam and present first systematic investigations. The interferometer is a typical Ramsey-Bordé setup [1], which makes use of the transition between the ground state $X \ ^1\Sigma_g^+$ and the long living electronically excited state $b \ ^3\Pi_u$.



This transition is observable due to coupling of the states b and $A \ ^1\Sigma_u^+$. To get accurate coupling coefficients to calculate the lifetimes of the perturbed triplet state, we investigated both states spectroscopically and performed a deperturbation analysis together with previously known data [2,3]. Moreover, we fitted new sets of Dunham parameters for both states.

We were able to resolve the hyperfine structure of the b state for the first time. It is mainly due to the magnetic dipole interaction, but line shape fits indicate an additional influence of the electrical quadrupole interaction. The coupling coefficients obtained from the deperturbation analysis allow the interpretation of the rotational dependence of the hyperfine splitting.

With the interferometer setup it is now possible e.g. to increase the accuracy of the measurement of the b state's hyperfine structure. For the future

we plan to study the influences of cold collision between the molecules and the residual potassium atoms in the beam. For this purpose it is important to increase the interferometric sensitivity. Therefore, we will change to a ground state interferometer applying STIRAP-transitions between vibrational levels as mirrors and beam splitters (life times several ms).

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QUANTUM BEAT MEASUREMENT OF THE MAJORANA EFFECT IN A MOLECULE

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By means of coherent spectroscopy in the time domain (quantum beat spectroscopy) we investigated the dynamics of magnetic moments associated with molecular hyperfine levels when exposed to a rapid (200 ns) field inversion. By excitation with a circularly polarized laser pulse ($\tau \sim 3$ ns), oriented $^{13}\text{CS}_2$ molecules were prepared in a cold beam. This excitation took place in a weak magnetic field ($B = 5.4$ G), whose direction was subsequently reversed. The initially created coherences among the excited hf levels were conserved after field reversal and thus could be used to characterize the changes in the level structure. It turned out that the process corresponds to a "Majorana spin-flip" where the magnetic moment reverses its orientation relative to the direction of the magnetic field.

**NUCLEAR QUADRUPOLE EFFECTS ON THE PRESSURE
BROADENING OF CH₃I IN THE $\nu_6=1$ EXCITED STATE**

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The collisional broadening coefficients of methyl iodide were measured for rotational transitions in the $\nu_6=1$ excited vibrational state. A Doppler-free double-resonance technique using collinear infrared and mmwave radiations allowed the accurate determination of the broadening parameters for all the hyperfine components of the ($J=10-9$, $K=9$) rotational multiplet. An evident dependence on the F quantum number was observed and this result is perfectly consistent with a theoretical model allowing calculations of collisional broadening and coupling for the hyperfine components.

ROTATIONAL SPECTRA OF ^{13}C AND ^{15}N ISOTOPOMERS
OF CYANOACETYLENE (HC_3N) IN THE GROUND AND
VIBRATIONALLY EXCITED STATES

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The rotational spectra of the astrophysically very important HC_3N -isotopomers in their ground and vibrationally excited states have been recorded extensively in the Cologne laboratory in the 2 mm region. Selected transitions of some vibrationally excited states have been measured up to 540 GHz. ^{13}C isotopomers were synthesized via DC discharge of acetylene and H^{13}CN . This leads mainly to the formation of the species HCC^{13}CN but also to an enrichment of ^{13}C in the remaining positions. Therefore, all monosubstituted ^{13}C isotopomers were easily detectable in the ground and various vibrationally excited states. The ^{15}N isotopomer was investigated in natural abundance.

Furthermore, rotational transitions of four doubly substituted isotopomers could be detected for the first time, namely $\text{H}^{13}\text{C}^{13}\text{CCN}$, $\text{H}^{13}\text{CC}^{13}\text{CN}$, $\text{HC}^{13}\text{C}-^{13}\text{CN}$, and $\text{HCC}^{13}\text{C}^{15}\text{N}$, not only in the ground but partly even in vibrationally excited states.

Work is in progress to extend the measurements into the THz region.

TERAHERTZ SPECTROSCOPY OF THE DIATOMIC MOLECULES SH, PH, AND NO

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Diatomic molecules are of special interest for both laboratory and astrophysical investigations. Pure rotational transitions of SH, SD, PH, and NO have been measured in the terahertz region and will be presented.

The $N = 2 \leftarrow 1$ transition of PH ($^3\Sigma^-$) has been recorded completely resolved in fine and hyperfine structure in the frequency region of 927 – 1067 GHz.

The rotational terahertz spectra of SH have now been completed and we present for the first time measurements of the deuterated species SD and ^{34}SD . The investigation of the transition $J = \frac{3}{2} \leftarrow \frac{1}{2}$ ($^2\Pi_{\frac{1}{2}}$) of SH allows an accurate frequency prediction for the $J = \frac{5}{2} \leftarrow \frac{3}{2}$ ($^2\Pi_{\frac{3}{2}}$) transition. The $^2\Pi_{\frac{3}{2}}$ electronic state is lower in energy and therefore, due to the Boltzmann distribution, favorable for observations of this species in cold interstellar clouds.

For nitric oxide, NO, measurements of highly excited J -transitions up to 1.08 THz allowed a detailed analysis of the uncoupling behaviour of the spin and the electronic angular momentum from the molecular axis. The partial decoupling of the electronic spin from Hund's case (a) to Hund's case (d) has clearly been recognized.

MICROWAVE SPECTRUM, CONFORMATIONAL
EQUILIBRIUM AND QUANTUM CHEMICAL
CALCULATIONS OF URETHANE (ETHYL CARBAMATE)

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The microwave spectrum of urethane ($\text{H}_2\text{NCO}_2\text{CH}_2\text{CH}_3$) has been investigated in the 16.5 - 56.0 GHz spectral region at room temperature. Two rotamers denoted **Conformer I** and **Conformer II** were assigned. The C=O and -O-CH₂ bonds are oriented in the *syn* conformation in both these rotamers. The H₂NCO₂CC atoms are co-planar in **Conformer I** with the *methyl* group *anti* to the C_{carbonyl}-O bond. The *ethyl* group is rotated 98° in **Conformer II** from the position it has in **I**.

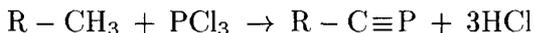
Conformer I is found to be 0.5(5) kJ mol⁻¹ more stable than **II** by relative intensity measurements. The ground vibrational state was assigned for **I**, whereas the ground and one vibrationally excited state were assigned for **II**.

The microwave work has been assisted by *ab initio* computations at the MP2/cc-pVTZ level of theory, as well as density theory calculations at the B3LYP/6-31G*

MILLIMETER-WAVE SPECTROSCOPY OF
PHOSPHA-ALKYNES: HC₃P AND NC₂P

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The millimeter-wave spectra of the unstable species HC₃P and NC₂P have been observed using a source-modulation spectrometer. The phospho-alkynes compounds were produced following the high-temperature route previously suggested by Kroto^a:



(with R = HC≡C- or N≡C-). The stable precursors were continuously flowed through a quartz pyrolysis tube heated to 1200°C, and the resulting products were then passed directly through the 3 m long, 10 cm i.d. free space cell of the spectrometer. Accurate values of rotational and centrifugal constants were determined for ground and several excited vibrational states.

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HIGH RESOLUTION ANALYSIS OF THE $3\nu_3$ AND $2\nu_1 + \nu_3$ BANDS OF NITROGEN DIOXIDE BY FOURIER TRANSFORM SPECTROSCOPY

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Long-path high resolution Fourier transform spectra of nitrogen dioxide has been measured in the $2\mu\text{m}$ region at the University of Denver. This has facilitated a new, extensive study of the $3\nu_3$ and $2\nu_1 + \nu_3$ bands. The energy levels of this molecule have been analysed using a Hamiltonian model that accounts for both the vibrational -rotational resonances and for the spin rotation interactions.

This work was motivated by the analysis of Kerridge and Remsberg ^a of the results from the Limb Infrared Monitor of the Stratosphere (LIMS) instrument. They suggested that Non Local Thermodynamical Equilibrium (NLTE) may result in emission due to hot bands of NO_2 . It is surmised that in the analysis of higher spectral resolution data of future remote sensing instruments, such as MIPAS, the NLTE emission of such hot bands may be of significance in the interpretation of the resulting data. This work complements the existing $2\nu_3 - \nu_3$ linelist ^b, to allow for a more accurate description of the NLTE effects.

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HIGH RESOLUTION ANALYSIS OF HDCO IN THE 10 μm REGION

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Using new Fourier transform spectra recorded at high resolution at Giessen, it has been possible to perform an extensive study of the ν_5 , ν_6 and ν_4 bands of the HDCO isotopic species of formaldehyde in the 900-1400 cm^{-1} spectral range. The analysis of these three bands was performed using the ground state parameters of Bocquet et al.^a and, for the ν_5 and ν_6 bands, starting from the results obtained previously in the same spectral region by Allegrini et al.^b For the ν_5 band (CHD rocking) and ν_4 band (out of plane bending) both A- and B-type transitions were observed, while the ν_6 band (out of plane bend) involves C- type and forbidden transitions. At a first step, the energy level calculation was performed using the model previously used by Allegrini et al.: i.e. for the v- diagonal blocks a Watson A-type Hamiltonian in Ir representation and for the $\nu_5 \leftrightarrow \nu_6$ off- diagonal blocks A- and B- type Coriolis operators. The final calculation was performed by taking also into account the weaker Coriolis A-type resonance involving rotational levels of the ν_6 and ν_4 interacting states.

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**INFRARED STUDY ON THE PAPE BAND $(\nu_6 + \nu_8)^0$ AND
THE HOT BANDS $\nu_6 + \nu_8 - \nu_8$ OF CD_3CN**

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The infrared spectrum of CD_3CN around 1380 cm^{-1} has been studied at a resolution of 0.0040 cm^{-1} . In this region the combination of two perpendicular fundamentals ν_6 and ν_8 is located. In the spectrum only the parallel component was observed although the path length was 150 m and the pressure 0.5 Torr. In this PAPE type band 1340 lines were assigned in 17 sub-bands. The vibrational ℓ -doubling and -resonance together with strong effects of rotational ℓ -resonances with the perpendicular component of the same vibrational level were observed. In addition, the Coriolis resonance with $\nu_3 + \nu_8$ and certain Fermi-type perturbations complicated the analysis. To get better understanding both the hot bands $(\nu_6 + \nu_8)^0 - \nu_8$ and $(\nu_6 + \nu_8)^2 - \nu_8$ were assigned (1508 lines) and analyzed together with the PAPE band. In the hot band $(\nu_6 + \nu_8)^0 - \nu_8$ the Q branch PQ_1 around 1049.5 cm^{-1} was found to have a doublet structure and the splitting in the sub-band gave direct information about the vibrational ℓ -doubling. The splitting of $K\Delta K = 1$ sub-band in $(\nu_6 + \nu_8)^2 - \nu_8$ giving rise to two families of lines was detected, too. In the calculations attention was paid to the main features of the PAPE problem. Higher order fitting parameters were avoided to keep the results reliable. The standard deviation $2.7 \times 10^{-3}\text{ cm}^{-1}$ was attained.

STUDY OF THE GROUND AND LOWEST VIBRATIONAL STATES OF THE $^{13}\text{CH}_3\text{D}$ MOLECULE

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High resolution spectrum of the natural mixture of the ^{12}C and ^{13}C species of the CH_3D molecule which was recorded with the Bruker IFS 120 HR (Oulu, Finland) in the region of $820 - 1750 \text{ cm}^{-1}$ (pressure - 1.12 Torr; path length - 41.6 m) shows the presence of numerous and strong transitions which can not be assigned to the $^{12}\text{CH}_3\text{D}$ molecule. As the analysis shown, they are the lines of the $^{13}\text{CH}_3\text{D}$ species (more than 1450 lines have been assigned to the ν_3 , ν_5 , and ν_6 bands of the $^{13}\text{CH}_3\text{D}$ with the values of quantum numbers $J_{\text{max}} = 18$ and $K_{\text{max}} = 12$).

Rotational analysis both of the ground, and of the ($\nu_3 = 1$), ($\nu_5 = 1$), and ($\nu_6 = 1$) excited states was made, and the spectroscopic parameters of all four vibrational states were determined. Resonance interactions between the states ($\nu_3 = 1$), ($\nu_5 = 1$), and ($\nu_6 = 1$) have been taken into account. In this case, the parameters of the $^{12}\text{CH}_3\text{D}$ species were used as the initial approximations and then were fitted. Values of unfitted parameters were fixed to the values of corresponding parameters of the $^{12}\text{CH}_3\text{D}$ molecule. Obtained parameters reproduce the initial rotation-vibration energies with the accuracies closed to the experimental uncertainties and explain $a_1 - a_2$ splittings with the values of quantum number $K^{\text{upper}} = 1, 2, 3, \text{ and } 4$.

**TUNNELING-ROTATION TRANSITION OF
MALONALDEHYDE OBSERVED IN THE
SUBMILLIMETER-WAVE REGION**

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Malonaldehyde has an intramolecular hydrogen bond, and the proton involved moves between the two equivalent potential minima by tunneling through the potential barrier. Previous microwave studies, e.g. Ref. [1], have reported the observation of pure rotational lines for each tunneling doublet component, 0^+ and 0^- . From the analysis of the perturbation between the doublet, the energy separation of the doublet was predicted to be 647 GHz.

In the present study, we have determined directly the energy separation, by observing the direct transitions between the tunnel doublet. The spectra have been recorded by the NAIR terahertz spectrometer, in the frequency region from 643 GHz to 651 GHz. Total 43 lines have been assigned to the *a*-type *Q*-branch transitions between the tunnel doublet, $0^- \leftarrow 0^+$.

The line intensities of those tunneling-rotation transitions are weaker than the pure rotational *b*-type transitions in this frequency range by two orders of magnitude. In the first step, we have assigned those pure rotational transitions as much as possible, and analyzed them to improve the prediction frequencies for the tunneling-rotation transitions. On the basis of the improved predictions, we were able to assign the weak tunneling-rotation transitions. The energy separation obtained in this study is in a good agreement with that given in the previous MW work[1].

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THE ν_1 AND ν_3 BAND OF ND₃

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The hindered inversion at the pyramidal nitrogen atom is among the classic problems in intramolecular dynamics including in particular tunneling dynamics and the possibility of molecular chirality with appropriate substitution [1–4]. Ammonia and its isotopomers have been prototype molecules for the study of inversion at the pyramidally substituted nitrogen atom for many years [1]. Most of the spectroscopic studies have concerned the main isotopomer NH₃. High resolution (0.004 cm⁻¹ instrumental bandwidth) interferometric Fourier transform infrared spectra of ¹⁴ND₃ were obtained on a BOMEM DA002 spectrometer under essentially Doppler limited conditions[5]. We report the analysis of the ND₃ stretching fundamentals with band centers at $\tilde{\nu}_1^0 = (2420.109 \pm 0.001)$ cm⁻¹ and $\tilde{\nu}_3^0 = (2563.9161 \pm 0.0005)$ cm⁻¹ with inversion tunneling splittings $\Delta\tilde{\nu}_1^0 = 0.5412$ cm⁻¹ and $\Delta\tilde{\nu}_3^0 = 0.0209$ cm⁻¹. About 50 parameters of the effective hamiltonian for this band system could be determined accurately. Assignments were established with certainty by ground state combination differences [6]. The results are important for and are discussed in relation to the mode selective inhibition of inversion at the nitrogen atom by exciting ND stretching vibrations as well as treatments of isotope effects on inversion of ammonia by means of effective hamiltonians as well as true molecular hamiltonians on high dimensional potential hypersurfaces. We also present results on the isotopomers NHD₂ and NH₂D.

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MEASUREMENT OF NEAR-INFRARED AND VISIBLE ABSORPTION CROSS-SECTIONS OF WATER VAPOUR

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Absorption spectra fully covering the 9,000 to 15,800 cm^{-1} (1.1 μm to 630 nm) region have been recorded for pure water vapour and air-broadened mixtures using the high resolution Bruker IFS 120HR Fourier transform spectrometer and coolable long pathlength absorption cell (LPAC) at the RAL Molecular Spectroscopy Facility. The recording of accurate, high quality data was made possible by a number of experimental developments including the installation of high reflectivity 'White' optics and humidity sensors in the LPAC, and fully evacuated optical paths outside of the LPAC. Measurements were made at a spectrometer instrument resolution (0.9/maximum optical path difference) of 0.03 cm^{-1} , optical pathlengths of 32, 256, and 512 metres, and sample temperatures of 253 and 294 K. A complete assessment of the experimental uncertainties in the measurements has been made.

Applications of this data include the interpretation of atmospheric remote sensing observations e.g. by the European Space Agency's satellite-based instruments Global Ozone Monitoring Experiment (GOME and GOME-2) and SCanning Imaging Absorption SpectroMeter for Atmospheric Cartography (SCIAMACHY), and shortwave atmospheric radiative transfer studies.

INFRARED LASER SPECTROSCOPY OF THE ν_4 AND ν_6 FUNDAMENTALS OF *cis*-CHCl=CHF

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Cis-1-chloro-2-fluoroethylene has been synthesized, and the gas-phase infrared spectra have been analyzed in the ν_4 ($\simeq 1335\text{ cm}^{-1}$) and ν_6 ($\simeq 1062\text{ cm}^{-1}$) regions, at Doppler limited resolution, using a tunable diode laser spectrometer. The measurements were carried out at 240 K in order to minimize hot band contributions.

These vibrations of symmetry species A' give rise to **a/b** hybrid bands with contributions from both the components mainly in the ν_6 fundamental. Since the asymmetry parameter κ is -0.895 , this molecule approaches to a prolate symmetric top and the structure exhibits patterns characteristic of parallel (**a**-type) and perpendicular (**b**-type) bands.

The rovibrational analysis led to the identification of about 1900 ($J \leq 71$, $K_a \leq 20$) and 2000 transitions ($J \leq 84$, $K_a \leq 19$) for the ν_4 and ν_6 fundamentals, respectively, of the ^{35}Cl isotopic species. Different excited state perturbations occur throughout the ν_6 band, caused by the first order **b**-type Coriolis resonance with the $\nu_9 + \nu_{10}$ vibrational state. From the subband analyses there is evidence that also the ν_4 vibration is slightly influenced by Coriolis resonance and the $3\nu_{12}$ overtone seems to be responsible for the observed perturbations.

Using Watson's A-reduction Hamiltonian in the I^r representation, accurate spectroscopic constants for both the ν_4 and ν_6 fundamentals have been obtained. Parameters for the $\nu_9 + \nu_{10}$ perturber were also determined from the interaction effects near the observed crossings in the ν_6 band.

Spectra, details of the interpretation, and results obtained from the analysis will be presented.

UPDATED ELECTRIC DIPOLE MOMENT FUNCTION FOR CARBON MONOXIDE

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We report a new experimental determination of the electric dipole moment function (EDMF) for the X state of CO which will be useful for the calculation of rovibrational intensities in high-temperature sources. All of the rovibrational line intensities currently listed for carbon monoxide in the HITRAN and HITEMP data bases have been computed from an (EDMF) reported 15 years ago [1]. Line intensity and frequency data used as input for the determination of that EDMF is even older. New line intensity measurements on the ($v = 0 \rightarrow v = 3$) band of CO, reported by Henningsen *et al.* [2] and Picqué and Guelachvili [3], indicate that the HITRAN values are about 8 percent too high. This result has been confirmed by us [4] and along with new results on the fundamental and first overtone bands is incorporated in the new EDMF determination. The Padé approximant representation of the EDMF was determined using experimental absolute and relative intensities and the appropriate numerically computed wave functions.

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COLLISION INDUCED SPECTRA IN THE FUNDAMENTAL OF N₂ AND O₂

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New experimental and theoretical studies of the collision induced fundamental absorption spectra of N₂-O₂ and O₂-N₂ pairs, where the first molecule makes the vibrational transition, will be presented for a range of temperature appropriate to the Earth's atmosphere.

Most of the absorption arises from long range quadrupolar mechanisms for which accurate matrix elements are available. It will be shown that a good global fit to the temperature dependent integrated intensities can be achieved for all the available data, i.e. the present ones and those previously obtained for N₂-N₂ and O₂-O₂, provided that a short range component to the dominant quadrupolar induction mechanism is taken into account.

Using the parameters thus determined, we then calculate the spectral profiles, assuming the lineshape calculated quantum-mechanically for N₂. The agreement between theoretical and experimental profiles

is good. Small discrepancies, which we attribute to the neglect of linemixing and higher order induction mechanisms still remain in the wings of the bands.

Similarly, structured absorption features superimposed on the broad collision induced bands have been observed, even at room temperature, corroborating previous observations in N₂-N₂ and O₂-O₂.

Here too, difference spectra obtained by subtracting the theoretical results from the observed data appear quite similar to those previously obtained for N₂-N₂ at about 80K. These spectra can be interpreted in terms of transitions between metastable (quasi-bound) states of van der Waals complexes.

Indeed, for $(\text{N}_2)_2$, spectral intensities and frequencies of these particular transitions are available and can be used, without any modification, to calculate synthetic profiles

INFLUENCE OF THE TRANSLATIONAL MODELLING ON THE FAR WING RAMAN SCATTERING SPECTRUM

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A set of available experimental data for the far wings of anisotropic Raman and isotropic Rayleigh spectra of nitrogen^{a,b} manifests a purely binary collision regime accompanied by an exponential dependence of measured intensities on the frequency.

To describe these spectra, in our previous study^c the traditional Energy Corrected Sudden (ECS) model^d was generalized to the case of non-Markovian collisions resulting in the frequency-dependent relaxation matrix which satisfies all general relations: both matrix and time reversal symmetries as well as double-sided sum rules. With the adiabaticity factor in traditional lorentzian form

$$\Omega(\omega) = (1 + \omega^2 t_c^2 / 6n)^{-n} , \quad (1)$$

(where t_c is the effective collision duration) this modelling led to a quite satisfactory description in the whole frequency range (from 20 to 620 cm^{-1}) without any additional parameter. But a slight overestimation of the scattered intensities was obtained at high frequencies and was attributed to the use of Eq.(1) even in the very far wing.

Here we present a similiar calculation with a new adiabaticity factor based on a typical model for collision induced translational spectrum^e

$$\Omega(\omega) = \exp a(1 - \sqrt{1 + \omega^2 t_c^2 / 6a}) .$$

This dependence remains quasi-lorentzian at low frequencies and insures an exponential decreasing at high ones. Moreover, it needs only one additional parameter a , which manages more physical high frequency behaviour.

Successive fittings of this new parameter over the experimental $Q_{iso}(J)$ linewidths show, as expected, that the low-frequency part of the spectrum is insensitive to its value. In contrast, the slope of the high frequency linear

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part is greatly influenced by it giving the best agreement with experiment for $a = 1.5$.

Due to the relative simplicity and the universal character with regard to the tensorial rank of the spectrum, this model is promising for its application to other molecular systems and spectroscopies.

**INHOMOGENEOUS PROFILES FROM THE DOPPLER TO
THE COLLISIONAL REGIME : ANALYSIS OF H_2 RAMAN
SPECTRA WITH A UNIFIED MODEL**

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It is very well-known that velocity-changing collisions lead to the so-called collisional confinement narrowing or Dicke effect [1] at low density. Different approaches [2–3] based either on soft or hard collision approximations have been extensively used to modelize the experimental lineshapes. At higher density, the role of the speed distribution of the collisional width and shift has been evidenced [4–7]. This distribution is partially reduced by the collisionally induced speed-classes exchange, leading to specific spectral features. In particular, the observed width and shift exhibit a non-linear dependence vs. the perturber concentration and the profile is asymmetrical.

Very recently, B. Lance and D. Robert [8] have proposed a unified model, which accounts for the two above effects, and thus applies from the Doppler up to the collision regime. Measurements in $H_2 - Ar$ mixtures are performed by Stimulated Raman Gain Spectroscopy in order to validate this approach. For densities varying between 0.2 and 11 amagat and three temperatures (296, 795 and 995 K), we demonstrate the high consistency of the unified model with experiments [9]. *All* spectra recorded can be described using a *unique* set of characteristic parameters-laws for all the density and temperature ranges.

Their analysis in terms of the lineshape model should allow us to get a refined understanding of all the physical mechanisms underlying the observed features, particularly in the mid-density region relative to the Dicke minimum, where both confinement narrowing and speed distribution of width and shift play a significant role.

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STUDY OF ROTATIONAL RELAXATION IN LINEAR MOLECULES WITH FEMTOSECOND RAMAN INDUCED POLARIZATION SPECTROSCOPY

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A Raman induced polarization spectroscopy^a (RIPS) apparatus has been constructed in Dijon. This technique is derived from rotational coherence spectroscopy (RCS) whose principle relies on the coherent excitation of rotational states with picosecond or femtosecond lasers. The rotational quantum beats of the superposition states lead to transient alignment. In RIPS, the excitation and the detection of the transients are obtained via stimulated Raman effect. The present experiment is based on a high power chirped pulsed amplified Ti:Sapphire femtosecond laser. This system, operating at 20 Hz repetition rate, delivers 5 mJ energy for a 80 fs pulse duration. The 800 nm pump and probe beams, delivered by the same laser, are mixed at a small angle in a low pressure one meter long gas cell. The probe laser, polarized at 45° with respect to the vertically polarized pump laser, passes through two perpendicular aligned polarizers placed before and after the cell. The detection of the signal is ensured by a photomultiplier. The delay between the pump and the probe lasers is varied with a corner cube retro-reflector mounted on a motorized linear stage.

Experiments have been conducted at room temperature and at pressure below 2 atm with pure N₂ and CO₂ gas as a test of the apparatus. Both homodyne and optically heterodyned detection (OHD) have been used. Calculations of the signal as a function of the pump-probe delay have been performed taking into account the pulse duration of the laser, the rotational dependence of the dephasing rates and the small instantaneous electronic Kerr effect. The observed decay and shape of the rotational quantum beats are in good agreement with the calculations. We used several sets of dephasing coefficients corresponding to the diagonal part of the collisional rotational relaxation matrix. This matrix was chosen among available models derived from frequency domain studies (fitting and scaling laws). A comparison between the models will be presented.

The extension of the measurements in mixtures such as CO₂-Ar and CO₂-He at higher pressure is in progress.

^aM. Morgen et al., Chem. Phys. Lett. **209**, 1, 1993

**QUANTUM INTERFERENCE IN A MOLECULAR
IONIZATION CONTINUUM****E. HERTZ, O. FAUCHER, B. LAVOREL, R. CHAUX**
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We report on the observation of a coherent modification of the lowest $v = 0$ ionization continuum of NO. The effect is achieved through the technique of laser-induced continuum structure (LICS), which has former been used with success for the manipulation of atomic continua and dissociative continua. In the present experiment, the continuum is dressed by electromagnetically embedding the $D^2\Sigma^+$ and $M^2\Sigma^+$ Rydberg excited states with two synchronized laser pulses of different frequencies (ν_1 and ν_2). Ionization of the ground state population is achieved by a two ν_1 -photon resonance via the $D^2\Sigma^+$ state. With a proper choice of the relative laser frequencies, a four-photon resonant Raman coupling is selected to connect a single rotational ground level to the M state. The different ionization channels, unavoidable in a two-color multi-photon scheme, are resolved by measuring the kinetic energy of the outgoing electrons. The photoelectron spectrum shows the presence of three decay channels owing to the ionization of the ground level at frequency $2\nu_1 + 2\nu_2$, $2\nu_1 + \nu_1 - \nu_2 + \nu_1$, and $2\nu_1 + \nu_1$. Among these channels, only the last one produces interference because of its degeneracy with the $2\nu_1 + \nu_1 - \nu_2 + \nu_2$ and $2\nu_1 - \nu_2 + \nu_1 + \nu_2$ companion processes. Monitoring photoelectrons of proper energy, while tuning the ν_2 -frequency, reveals a window resonance laser induced in the continuum spectrum. The modification of the ionization rate is interpreted in terms of coherent interaction of the molecular system with the electromagnetic field.

SPECTROSCOPIC AND THEORETICAL STUDY OF THE CH STRETCHING JET-COOLED SPECTRUM OF CYCLOPENTENE

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Cyclopentene is of interest for some time as a model system to investigate the contribution of the low hindering large amplitude ring-puckering motion to the intramolecular vibrational energy redistribution.

Several previous studies realized with the -4h and -3h monohydrogenated derivatives have led to a good modelling of the effective coupling between the ring-puckering motion and the CH stretching vibration till the fifth overtone. The coupling via Fermi resonance with combination states involving deformation of the angles adjacent to the initially excited CH bond are also modelled [1-3].

Recently, the study of the -3,3,4,4 d₄ derivative has allowed a comparison between the behaviour of a CHD and a CH₂ chromophoric group and a refinement of the coupling parameters [4].

We now extend this study to the fully hydrogenated molecule with three neighbouring CH₂ methylenic groups. The FTIR spectrum was recorded between 3000 and 2800 cm⁻¹ in a supersonic expansion jet of cyclopentene/Argon mixture with a resolution of 0.1 cm⁻¹ on a BRUCKER 120.

The spectrum is analysed with a similar theoretical treatment as that used for the other isotopic derivatives and compared to the room temperature spectrum. The differences observed between the jet cooled and room temperature spectra can be understood.

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**CLASSICAL INTERPRETATION OF THE ROTATIONAL
STRUCTURE OF THE $\nu_6 = 1$ VIBRATIONAL LEVEL
OF $\text{Mo}(\text{CO})_6$**

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The triply degenerate ν_6 mode of the octahedral $\text{Mo}(\text{CO})_6$ molecule presents unusual features, related to the low value of the Coriolis constant^a. The first-order Coriolis coupling usually splits a triply degenerate vibration state into three distinct vibrational components; the number of levels in each branch is given by $2R + 1$, where R equals $J \pm 1, J, J \mp 1$ for respectively the upper, the middle and the lower branch. In our case, the following pattern can be seen :

J values	$J < 8$		$J > 8$	
branch	R	number of levels	R	Number of levels
upper branch	J-1	2J-1	J+2	2J+5
middle branch	J	2J+1	J-3	2J-5
lower branch	J+1	2J+3	J+1	2J+3

Two structures are clearly visible, whether J is less or more than 8. A redistribution occurs for $J \sim 8$: six levels are seen to leave the middle branch and go to the upper branch.

Our work is based on a classical treatment of the angular momentum, i.e. we have substituted the quantum operators \widehat{J}_α , ($\alpha = x, y, z$), by their classical limit J_α . The quantum problem is therefore reduced to the diagonalization of a small matrix, whose eigenvalues $E^J(\theta, \phi)$ are the rotational energy surfaces (RES)^b.

Symmetry arguments are used to find the critical orbits on the surface of the RES. Energy and stability are computed on these stationary points^c. The use of a classical momentum is shown to be a useful tool when discussing the dependence of the rotational structure with J, for example the type or the number of quasi degenerate levels (clusters).

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^cD.A. Sadovskii and B.I. Zhilinskii. *Mol. Phys.*, **65**, 109-128 (1988).

The redistribution phenomenon is then studied. It is pointed out that two RES are degenerated for $J \sim 8$ in some particular space directions : a contact point, which corresponds to a singularity, can therefore be observed in these directions. A simple model is built, allowing us to exhibit the two parameters responsible for the redistribution, to demonstrate the stability of this phenomenon under small perturbation and to investigate the correspondence between quantum energy levels pattern and classical energies of critical orbits.

We hope that our poster will demonstrate the possibility of a classical qualitative and even quantitative interpretation of effective rovibrational hamiltonians.

**EFFECTIVE QUADRUPOLE COUPLING OPERATOR FOR
QUASIDEGENERATE VIBRATIONAL STATES OF
POLYATOMIC MOLECULES IN THEORY OF LINKED
ORDERING SCHEMES OF ROVIBRATIONAL
INTERACTIONS**

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The contribution have been devoted the construction of effective quadrupole coupling operator for quasidegenerate vibrational levels of polyatomic molecules and the reduction of the last. The indeterminacy problems of the parameters in the effective vibrational-rotational H_{VR}^{eff} and quadrupole W^{eff} Hamiltonians for the cases of accidental resonances linked with various groupings of vibrational-rotational interactions [problem of grouping uncertainty] are considered. The problem of the reduction of $H^{eff} = H_{VR}^{eff} + W^{eff}$ is discussed. The case of the Coriolis-type accidental resonances have been considered more detail. New representation of $H^{eff} = H_{VR}^{eff} + W^{eff}$ for isolated vibration levels in form of Lemma for rotational and pseudoangular vibrational momenta has been developed.

**THE PHOTOELECTRON SPECTRUM OF NO₂. AN
AB-INITIO MRD-CI STUDY**

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We report ab-initio MRD-CI electronic structure calculations of the NO₂⁺ cation. Bending potential energy curves are reported for ten singlet and eight triplet states. A cut of the potential energy surfaces along the asymmetric ON-O coordinate is also reported. Several of the calculated states are reported for the first time. A basis set of DZ + POL quality augmented with *s*- and *p*-type Rydberg functions was employed together with an extensive treatment of electron correlation. The vertical ionization spectrum of NO₂ is found in very good agreement with the experimental spectrum of Edquist et. al.. Singlet-triplet splittings are reported and compared with the measured values.

THE $RbCs$ $X^1\Sigma^+$ ELECTRONIC GROUND STATE. NEW SPECTROSCOPIC STUDY**C. FELLOWS^a, R. F. GUTTERRES^a,****J. VERGÈS** and **C. AMIOT**, *Laboratoire Aimé Cotton, Bât. 505, Campus d'Orsay, 91405, Orsay, France*; **A. P. C. CAMPOS**^a, *Laboratoire de Photophysique Moléculaire, Bât. 210, Campus d'Orsay, 91405, Orsay, France*

In this work a new spectroscopic investigation, on the $X^1\Sigma^+$ electronic ground state of the $RbCs$ molecule, is reported. This study is done by using Laser Induced Fluorescence combined with Fourier Transform Spectroscopy (LIF-FTS). More than 23,000 spectral data lines are used in a global linear reduction to molecular constants. With these new and improved molecular constants, the potential energy curve has been calculated by the Inverted Perturbation Approach (IPA). Accurate values for the dissociation energy and the long range parameters have been derived.

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**THE FOURIER TRANSFORM EMISSION SPECTRUM OF
THE $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$ ELECTRONIC TRANSITION OF N_2O^+**

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The Fourier Transform spectrum of N_2O^+ has been recorded at high resolution from a Penning ionization source *i*) at room temperature *ii*) and in a supersonic jet expansion. The rotationally cold spectrum exhibits sharp bands readily assigned by using the analysis results previously reported^b. Some weaker bands previously unassigned have been identified on the basis of recent ab-initio calculations^c. The rotational analysis of both spectra allow us to determine molecular parameters for a number of vibronic levels in $\tilde{X}^2\Pi_i$, where the Renner-Teller effect and Fermi interaction have been taken into account.

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^bJ. H. Calomon and F. Creutzberg, *Phil. Trans. R. Soc. A*, **277**, 157-189 (1974)

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HIGH RESOLUTION LASER SPECTROSCOPY OF THE $^{39}\text{K}^{85}\text{Rb}$ $1^1\Pi$ AND $2^1\Pi$ STATES

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High resolution spectra of the $1^1\Pi(v' = 13 - 69, J') \leftarrow X^1\Sigma^+(v'', J'')$ and $2^1\Pi(v = 0 - 13, J) \leftarrow X^1\Sigma^+(v'', J'')$ transitions of the $^{39}\text{K}^{85}\text{Rb}$ molecule have been measured by the technique of Doppler-free optical-optical double resonance polarization spectroscopy (OODRPS). Molecular constants of the $1^1\Pi(v = 13 - 69)$ and $2^1\Pi(v = 0 - 13)$ levels are determined, and potential energy curves are constructed by the RKR method. The obtained RKR potential of the $1^1\Pi$ state has a distortion at outer wall, which is originating from an avoid crossing of two $1^1\Pi$ states.

The perturbation between $1^1\Pi(v_1, J) \sim 2^1\Pi(v_2, J)$ levels are found from the energy shifts of the rotational levels. The line intensities are observed to change drastically around the J of maximum energy shift. These intensity anomalies can be explained by an interference effect, which occurs when two interacting levels have comparable transition moments from a common level.

A remarkable line broadening was observed for the transitions to the $1^1\Pi(v \geq 63)$ levels, and it is identified as originating from the predissociation to $\text{K}(4s^2S) + \text{Rb}(5p^2P_{1/2})$ atoms. From the analysis, the dissociation energies of the $X^1\Sigma^+$, $1^1\Pi$, and $2^1\Pi$ states are determined.

**DOPPLER-FREE HIGH RESOLUTION SPECTRAL ATLAS OF
IODINE MOLECULE 15,000 TO 19,000 cm^{-1}**

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The absorption spectrum of the iodine molecule in the 15000 - 19000 cm^{-1} region has been measured by applying the technique of Doppler-free laser spectroscopy. Each individual spectrum (approximately 0.52 cm^{-1} in range) consists of:

- 1) The frequency marks of the etalon which can be used to calculate the absolute wave number of a given hyperfine line of I_2 ;
- 2) The excitation spectrum of I_2 which is broadened by the Doppler effect;
- 3) The Doppler-free absorption spectrum of I_2 ;

All of which were measured simultaneously. The absolute frequency of a transition line in this region can be obtained with a standard deviation of 0.000054 cm^{-1} .

In addition to this printed document, this spectral data is available on an accompanying CDROM. Using this CDROM, it is possible to obtain the absolute wave numbers of all the hyperfine components in this atlas. This can be used to calibrate the absolute wave number of molecular transition lines with accuracy of approximately 0.0001 cm^{-1} .

DEVELOPMENT OF JET-COOLED SUPERSONIC CARBON CLUSTER SOURCES

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Small carbon clusters C_n ($n \leq 20$) can in principle exist in two isomeric forms in their electronic ground state, a linear chain and a cyclic ring structure. The linear structure is predicted to be most stable for clusters which contains less than 10 carbon atoms, whereas the ring structure is predicted to be more stable for larger clusters. Since the linear isomer has been confirmed for many small clusters up to C_{15} only few experimental data exist showing evidence for the ring structure. In order to study the structure of clusters by high resolution spectroscopy efficient supersonic cluster sources are strongly required.

In our setup, a quadrupole mass spectrometer with a range of 1 – 400 amu is used to control and optimize various types of supersonic jet carbon cluster sources. The optimum conditions for a laser ablation source have been obtained and the total amount of the clusters C_3 , C_9 , and C_{13} have been estimated by infrared absorption spectroscopy.

**MOLECULAR EVOLUTION DESCRIPTION AND
RESONANCE CALCULATING FOR ONE-DIMENSIONAL
QUANTUM SYSTEMS**

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New method for description of resonance positions and widths for quantum systems is described. This approach combines the main advantages of both the Complex Absorbing Potential methods and Stabilization Graphs technique. It is able to reproduce the resonance's characteristics very accurately and needs only minor calculating effort. The same basic idea may be implemented to describe long-time model system evolution avoiding the problems of wave-packet reflection from the grid/basis boundary. Applied to several model systems this technique manifests itself very effective.

This work has been supported by the Russian Fund of Fundamental Natural Sciences.

GROUND-STATE POTENTIAL ENERGY SURFACE OF OZONE DETERMINED FROM RO-VIBRATIONAL SPECTRA

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The effective ground-state potential energy surface (PES) of the ozone molecule has been obtained via a least-squares fit to an extensive set of experimental, high-resolution vibration-rotation data. This is done in two steps. In the first step, the approximate "Morse Oscillator Rigid-Bender Internal Dynamics" model for the kinetic energy part of the vibration-rotation Hamiltonian has been used. This allowed significant reduction of the CPU time and memory requirements of the least-squares fitting procedure and thus enabled us to include the largest sample of spectroscopic data used to date^a for this purpose. This potential function was then used as a starting approximation for the second step, which is to make a refined least-square fit using an exact-kinetic-energy Hamiltonian. The root mean square deviation of the fit of all available band centers observed at high-resolution is 0.09 cm^{-1} . This includes bands recently recorded and assigned in Reims and includes highly excited stretching and bending vibrations with $v_1 + v_2 + v_3$ up to 6. The physical consistency of the PES is confirmed by rotational, vibrational and isotopic extrapolations. The PES shows a physically meaningful long range behavior at the dissociation limit $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$: the calculated D_0 (1.056 eV), is in excellent agreement with the experimental value ($1.06 \pm 0.04 \text{ eV}$) recently measured in low energy electronic impact. The comparison of these two potential energy surfaces with those available in the literature and with *ab initio* calculations will be discussed.

Vl.G.Tyuterev, S.A.Tashkun, P.Jensen, A.Barbe, and T.Cours, 15-th HRMS Conference, paper M2, Prague 1998.

MULTI-CONFIGURATION LINEAR RESPONSE APPROACH TO THE CALCULATION OF PARITY VIOLATING POTENTIALS IN POLYATOMIC MOLECULES

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Parity violating potentials in polyatomic molecules may be of fundamental importance for molecular chirality including biomolecular applications [1]. The calculation of parity violating potentials has in the past been carried out in extensive series of papers mostly following the Hartree-Fock (SDE-RHF) framework of Hegstrom, Rein and Sandars [2,3]. The recent discovery of an increase of calculated parity violating energies in a framework based on a configuration interaction method with singly excited states (CIS-RHF) has led to a new understanding of the need for a systematic approach towards “electroweak quantum chemistry” [4,5]. We report the first application of the multi-configuration linear response (MCLR) method [6,7] to the calculation of parity violating potentials in polyatomic molecules [8]. This approach represents an important step towards a more reliable calculation of parity violating effects in molecules. We present results for the parity violating potentials in hydrogen peroxide as well as in twisted ethylene. The latter compound is known to be a biradicaloid, which can not be described accurately with the methods applied in previous studies. If time and space permit, we also present new results on biologically important molecules, as well as molecules that are useful for experimental studies of parity violation [1].

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HIGH RESOLUTION STIMULATED RAMAN SPECTRUM OF THE ν_2 Q-BRANCH REGION OF DIACETYLENE

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We present the analysis of the Raman spectrum of the ν_2 ($\Sigma_g - \Sigma_g$) Q-branch region at near Doppler resolution, recorded with the Stimulated Raman Spectrometer at Madrid. The ν_2 mode correspond to the symmetric $C \equiv C$ stretch. Besides the fundamental, the recorded region includes the rotationally resolved hot band $\nu_2 + \nu_9 - \nu_9$ ($\Pi_u - \Pi_u$). The two overlapped Q-branch $\nu_2 + 2\nu_9^0 - 2\nu_9^0$ ($\Sigma_g - \Sigma_g$) and $\nu_2 + 2\nu_9^{\pm 2} - 2\nu_9^{\pm 2}$ ($\Delta_g - \Delta_g$) also appear in this region but the spectrum is too congested to extract any information.

The upper states ν_2 and $\nu_2 + \nu_9$ are strongly perturbed. The fundamental state has a crossing at $J = 51$ with a gap of 0.7 cm^{-1} and another crossing at $J = 35$ with a much smaller gap of 0.09 cm^{-1} . Besides, several others crossings shifting only a couple of lines by a few 10^{-3} cm^{-1} can be seen once the effect of the main ones is taken into account.

The visible range of the hot band up to $J = 61$ shows no trace of upper level crossing, except for the line $J = 60$ of the f sub-band, which is slightly shifted to lower frequency. However, the analysis show that the upper state is strongly perturbed by a higher lying state with the interaction getting weaker as J increases.

An identification of the perturbing states has been attempted leading to an interaction scheme that involves a Fermi resonance through a quintic potential constant between ν_2 and the state $2\nu_3 + 2\nu_9^0$, which is in turn connected through rotational l -type resonance to $2\nu_3 + 2\nu_9^{2e}$. For the hot band, the same interaction is reproduced among states involving one more quanta of ν_9 . This scheme reasonably explains the observed features for both the fundamental and hot bands in common grounds, but the experimental data are not enough to rule out other interpretations, mainly owing to line overlapping and the fact that transitions to the unperturbed part of the interacting states are too weak to be observed.

**SOFTWARE FOR MEASURING LINE POSITIONS,
STRENGTHS AND WIDTHS FROM HIGH RESOLUTION
FOURIER TRANSFORM SPECTRA**

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Easy-to-use software has been written for processing high resolution Fourier transform spectra. This software can be run on any personal computer, Pentium type or equivalent. It only needs the ORIGIN software to be installed on the PC. The software can least-squares fit any portion of a spectrum to a sum of gaussian, Voigt or lorentzian profiles convoluted with a chosen apparatus function and it allows thus accurate determination of line positions, linestrengths and broadening coefficients.

The use of the software for treating different kinds of spectra will be demonstrated.

QUASI-LINE SPECTRA AND NH(ND) ISOMERISM IN METHYL DERIVATIVES OF ISOBACTERIOCHLORIN

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At 4.2 K the quasi-line fluorescence and fluorescence excitation spectra of the *cis* and *trans* forms of octamethylisobacteriochlorin (OMiBC) and its cyano substituted analogue (COMiBC) in polycrystalline *n*-alkane matrices have been obtained. The vibrational analysis of these spectra enabled, jointly with the data of the quasi-line spectra of porphin and octamethylporphin investigated earlier, qualitative interpretation of the vibronic spectra obtained.

Now it is established that the dark process of NH isomerism in free bases of porphyrins and chlorins occurs via the intermediate isomer with adjacent disposition of the NH protons, i.e. the process involves consecutive transformation of the *trans* form into the *cis* form and then again to the *trans* form. It is possible that the process of photoinduced NH isomerism is of the same character. At the same time, the intermediate *cis* form of free-base porphyrins and chlorins, and the intermediate step of the *trans-cis* process of the NH photoisomerism either, have not been detected experimentally.

In this communication, by an example of OMiBC and COMiBC, the results of the experimental investigations of one-proton processes of photoinduced *cis-trans* (*trans-cis*) NH(ND) isomerism are presented. On the basis of measured action spectra, for COMiBC data have been obtained on the correlation between the impurity centers (sites) of the *cis* form and the sites of the photoproduct (*trans* form). The absence of quasi-lines in the action spectra for most of the sites of the *trans* form of D₂-COMiBC is explained by the retardation of direct *cis-trans* photoreaction on deuteration of the central NH groups.

HYPERFINE STRUCTURES IN THE MICROWAVE SPECTRA OF STABLE SULFUR OXYFLUORIDES

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In an attempt to solidify our knowledge about the structure and dynamics of selected reference molecules, we have measured the microwave spectra of thionyl difluoride, F_2OS , sulfuryl difluoride, F_2O_2S , and sulfur oxide tetrafluoride F_4OS .

In the case of F_2OS we have observed the normal, ^{34}S , ^{33}S , and ^{18}O species in their vibrational ground states, and the v_3 , v_4 , and v_6 vibrational states of the normal isotopomer. All lines show ^{19}F spin-rotation and spin-spin coupling patterns. Earlier work had focused on centrifugal distortion effects. In this work we determined

- * the rotational and quartic centrifugal distortion constants of all isotopomers and bending vibrational states

- * ^{33}S quadrupole coupling constants and

- * ^{19}F spin-rotation and spin-spin coupling constants

F_2O_2S is the simplest neutral and stable member of the class of tetragonally bound sulfur compounds, and is isoelectronic to the sulfate dianion. It is an accidental near-spherical top (see also Poster on F_2O_2S). Earlier work had been somewhat restricted in terms of sensitivity and resolution. We have measured the spectra of the normal, ^{34}S , ^{33}S , and ^{18}O plus two transitions of the ^{17}O isotopomer, all in natural abundance. Moreover, we have observed vibrational satellites of the states v_2 , v_3 , v_4 , v_5 , v_7 , and v_9 . The ^{33}S and ^{17}O species show nuclear quadrupole patterns, and the analysis resulted in fairly precise values for the respective coupling constants.

In the case of the vibrational ground state and symmetric vibrationally excited states, even K_a transitions ($I=0$) appear as single lines, whereas odd- K_a transitions ($I=1$) show ^{19}F spin-rotation and spin-spin coupling patterns. For antisymmetric excited vibrational states, the reverse is true. For the $F_2^{18}O^{16}OS$ isotopic species, all transitions are split; because of the reduced symmetry both $I=0$ and $I=1$ exist.

As for the spectrum of F_4OS , analysis of the hyperfine structures is exceedingly difficult, since there are spin states $I_{ax} = I_{eq} = 0$, $I_{ax} = I_{eq} = 1$ (implying even K_c), and two states with odd K_c : $I_{ax} = 0$, $I_{eq} = 1$ and $I_{ax} = 1$, $I_{eq} = 0$. There are thus 10 or 6 states to consider, respectively. In addition, the magnitude of spin-rotation coupling is smaller (as it scales with the rotational

constants), whereas the mutual spin-spin coupling of all four fluorine nuclei becomes dominant due to reduced internuclear distances. We give, however, the first correct R-branch assignment for the normal isotopomer, and the first assignment whatsoever for the ^{34}S species.

Moreover we used the intensities of rotational transitions in different vibrationally excited states of F_2OS and $\text{F}_2\text{O}_2\text{S}$ to get information on vibrational beam temperatures. Quite unexpectedly, we have also observed the nuclear Zeeman effect produced by the coupling of the fluorine nuclei to the geomagnetic field.

THE TORSIONAL OVERTONE OF CH₃CF₃

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The weak, torsional overtone ($v_6 = 2 \leftarrow 0$) in CH₃CF₃ has been studied with Fourier transform spectroscopy at a resolution of 0.005 cm⁻¹ using an absorption path length of 80 m. A total of 436 lines were measured in this parallel band between 405 and 440 cm⁻¹ at a pressure of 1.5 Torr and a temperature of 196 K. The global data set consisted of the current frequency determinations and the 443 measurements with molecular beam, microwave and mm-wave methods analyzed by I. Ozier *et al.*^a A good fit was obtained by varying 18 parameters in a Hamiltonian that represented both the torsional effects and the sextic splittings. Improved effective values were determined for the height \tilde{V}_3 of the hindering barrier and the first order correction \tilde{V}_6 in the Fourier expansion of the potential function. In the earlier work, the large reduced barrier height led to high correlations among several of the torsional distortion constants. With the current measurement of the torsional overtone, many of these correlations are substantially reduced. The dipole function which characterizes the transition moment can be written as the product of a single effective dipole constant $\mu_{2,eff}^T$ and the appropriate off-diagonal element of p^2 , where p is the torsional angular momentum operator. From an intensity analysis of the spectrum, it has been determined that $\mu_{2,eff}^T = 0.414(30)$ mD.

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¹ I. Ozier, J. Schroderus, S.-X. Wang, G. A. McRae, M. C. L. Gerry, B. Vogelsanger, and A. Bauder *J. Mol. Spectrosc.* **190**, 324-340 (1998)

VIBRATION-TORSION-ROTATION ANALYSIS OF THE ν_{12} AND ν_{11} BANDS OF CH_3CF_3

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The two lowest-lying perpendicular fundamentals ($\nu_{12} = 1 \leftarrow 0$) and ($\nu_{11} = 1 \leftarrow 0$) have been measured in CH_3CF_3 with Fourier transform spectroscopy at a resolution of 0.00125 cm^{-1} . In each case, both the spectrum originating in the ground torsional state ($\nu_6 = 0$) and its first torsional hot band originating in the state ($\nu_6 = 1$) were studied. For the ν_{12} band, a total of 2697 transitions were identified; 31 A_1/A_2 sextic frequency splittings were measured for $\nu_6 = 0$. For the ν_{11} band, a total of 4485 transitions were identified, including 49 perturbation-allowed lines obeying the selection rules ($\Delta G = \pm 3$), where $G = k - l$. These lines became strong enough to be observed as a result of the resonance between levels with ($\nu_{11} = 1, l = -1; J, \nu_6 = 0, k = 11$) and ($\nu_{11} = 1, l = -1; J, \nu_6 = 0, k = 14$). No torsional fine structure due to σ -splitting was observed in either band.

For ($\nu_{12} = 1$), the current frequency measurements for ($\nu_6 = 0$) and ($\nu_6 = 1$) were analysed along with the 879 transition frequencies studied earlier^a within the ground vibrational state. A fit to within experimental accuracy was obtained using a Hamiltonian that represents both the torsional effects and the sextic interactions off-diagonal in k for the stack of torsional levels ($\nu_6 = 0, 1, 2 \dots$) in the state ($\nu_{12} = 0$) and the corresponding stack for ($\nu_{12} = 1$). No significant interstack interactions were detected. The standard deviation of the best fit was 0.00011 cm^{-1} . For ($\nu_{11} = 1 \leftarrow 0$), a similar analysis was carried out; in this case, the standard deviation of the best fit was 0.00009 cm^{-1} .

For each of the ($\nu_{12} = 1$) and ($\nu_{11} = 1$) vibrational states, the magnitude of the centrifugal distortion constant ϵ that characterizes the ($\Delta k = \pm 3, \Delta l = 0$) matrix elements has been determined. For each of the two vibrational states, the effective barrier height \bar{V}_3 has been obtained along with the l -doubling constant and the torsional dependence of the zeroth-order Coriolis constant.

Both torsional hot bands play an important role in determining the corresponding torsional parameters. When the ν_{12} and ν_{11} states are compared, it is found that the zeroth-order Coriolis constants are opposite in sign, as are the l -doubling constants.

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1 S.-X. Wang, J. Schroderus, I. Ozier, N. Moazzen-Ahmadi and A. R. W. McKellar, to be published.

**INVESTIGATION OF VIBRONIC SPECTRA OF
BISANTHENE AND HYPERICIN BY QUASI-LINE AND
FINE-STRUCTURE FLUORESCENCE SPECTRA METHODS**

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Bisanthene is a fundamental system for the hypericin molecules (molecules pertaining to natural biologically active pigments). The knowledge of spectral and photochemical properties of bisanthene and hypericin may serve as a basis for the study of more complicated photobiological and model systems involving aromatic chromophores.

In this work, for the first time, a totality of spectral-luminescent investigations of bisanthene has been carried out in a number of organic solvents at room, liquid nitrogen, and liquid helium temperatures. Special attention is paid to the quasi-line fluorescence and fluorescence excitation spectra of bisanthene in *n*-octane and *n*-hexane obtained at 4.2 K. The analysis of the normal mode frequencies in the S_0 and S_1 electronic states has been performed, and the results are juxtaposed with the earlier obtained data on the frequencies from the fine-structure fluorescence spectra of hypericin.

At liquid helium temperature, fine-structure fluorescence and fluorescence excitation spectra of hypericin embedded in an inorganic (tetraethoxysilane (TEOS)) and a hybrid organo-inorganic (vinyltriethoxysilane (VTEOS)) gel-matrices have been obtained. The vibrational analysis of the spectra has been carried out, and conclusions concerning the form of many modes have been drawn. Changes in activity of some modes in the S_1 state are attributed to the alteration of the strength of intramolecular hydrogen bonds on the electronic excitation, and the differences in the line intensities of the fluorescence spectra in the TEOS and VTEOS matrices - to different orientation of the hypericin molecules relative to the surface of the pores of these gel-matrices.

**RELATIONS AMONG LINEAR VIBRATIONAL
COORDINATES
FOR DIFFERENT MOLECULAR ELECTRONIC STATES**

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In accordance with general rulers, an electronic vibrational transition is an allowed one if a matrix element

$$R_{e'v'e''v''} = \int \Psi_{e'v'}^* \vec{M} \Psi_{e''v''} d\tau_{ev} \quad (1)$$

is unequal to zero. \vec{M} – a dipole moment with components M_x , M_y , M_z in a coordinate system associated with a molecule. But in the adiabatic approximation which is often used in solution of the electronic vibrational problem, Eckart axes for different electronic states of a polyatomic molecule, generally speaking, have no coincidence with each other due to difference in nuclear equilibrium configurations in these states. For the same reason linear vibrational coordinates q' and q'' are also different in these states. Because of this the integrand in (1) has the form

$$\Psi_{e'v'}^* \vec{M} \Psi_{e''v''} = \Psi_{e'}^*(r', q') \Psi_{v'}^*(q') \vec{M} \Psi_{e''}(r'', q'') \Psi_{v''}(q'')$$

where r' , r'' – corresponding electronic coordinates.

By this means before calculation (1), it is necessary to find relation between q' and q'' , after doing so the relation between r' and r'' can be easily found. It can be shown that the principal formula for this relation is as follows

$$\vec{a}_\tau' + m_\tau^{-1} \sum_i \sum_j T_{ij}' \vec{B}_\tau^{ij} q''^i = R(q'') \vec{a}_\tau'' + m_\tau^{-1} \sum_k \sum_l T_{kl}'' R(q'') \vec{B}_\tau^{kl} q''^k \quad (2)$$

here m_τ – mass of τ -th nucleus; \vec{a}_τ (with one and two primes) – radius vector for equilibrium positions of nuclei, \vec{B}_τ^l – Wilson vectors; T_{ij} – coefficients of inertia for the corresponding states; $R(q'')$ – the rotation operator of axes for the second electronic state with respect to the ones for the first electronic state in the process of vibrations. Angles among the principal axes for the nuclear equilibrium configurations in different electronic states are determined in usual way.

Presence of $R(q'')$ in (2) leads to non-linear dependence between q' and q'' , in this case one can write

$$q'^i = q_0^i + \sum_k \left(\frac{\partial q'^i}{\partial q''^k} \right)_0 q''^k + \frac{1}{2} \sum_k \sum_l \left(\frac{\partial^2 q'^i}{\partial q''^k \partial q''^l} \right)_0 q''^k q''^l + \dots \quad (3)$$

derivatives being calculated in the point $q'' = 0$.

Details of derivation and expressions of derivatives in (3) are described in the communication.

CALCULATION OF MOLECULAR PARAMETERS AND PREDICTION OF MICROWAVE TRANSITIONS OF CH_2DOD

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In this study we have calculated the torsional-rotational molecular parameters of asymmetrically deuterated methanol CH_2DOD . Matrix elements have been calculated up to the fourth excited torsional state. Using previously observed microwave (MW) transitions effective state dependent molecular parameters of the states involved have been evaluated. These parameters allowed the predictions for unobserved MW transitions to be made with a precision which will enable laboratory and astrophysical detection. The matrix elements and the torsional energies will be valuable in the assignment of far-infrared FIR absorption spectra and optically pumped FIR laser lines in this molecular isotopomer of methanol. The energy levels calculated might be an useful database to aid searches in the detection of asymmetrically substituted methanol at other frequencies in astrophysical sources which might be of significant importance for determination of parameters like the D/H ratio in the interstellar space.

POWERFUL OPO/OPA SOURCES FOR IR LIDAR TECHNOLOGY

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G. PASMNIK, *Passat Ltd., Canada*

Two different promising schemes of IR optical parametric oscillator/amplifier (OPO/OPA) sources to generate short (few nanoseconds) pulses with narrow a bandwidth and a high energy are described. These sources can be used for lidar application for remote sensing of atmosphere. The described schemes were studied experimentally as sources of tunable radiation in the $1.85 - 2 \mu\text{m}$ spectral range for following conversion by SRS in H_2 and D_2 into mid/far IR. A Nd:YAG laser was used as the pumping radiation source. A LiNbO_3 crystal served for nonlinear conversion of the pump radiation to the IR wavelength range in the OPO, while in the OPA two different crystals, LiNbO_3 and LiIO_3 , were tested.

Spectral parameters of the output radiation and its spatial structure are formed by the OPO, while the OPA is responsible for energy and temporal parameters. Such a division between the OPO and the OPA allows us to use an OPO scheme with an intracavity Fabry–Perot etalon. To prevent the pump wave from passage through the etalon, the OPO cavity is designed in a “L” shaped form. The tuning of the OPO/OPA output wavelength is attained by rotation of nonlinear crystals. Both OPO/OPA schemes can provide the bandwidth of the output radiation of about 0.1 inverse centimeter and the energy level up to 200 mJ, which results in 20 mJ pulse energy in the $8 - 10 \mu\text{m}$ spectral range.

Depending on the pulse pump duration it is necessary to use different OPO schemes. One of the described schemes can be used for the pumping radiation with the pulse duration of 6 – 8 ns. To provide OPO excitation and narrow bandwidth generation, a multipass design is implemented. In another case of the long pump pulse duration (20 – 30 ns), for the short pulse output OPO radiation (2 – 3 ns) the scheme with compression of the pumping radiation is used. The pump pulse transmitted trough the OPO is splitted into two parts. One portion is then reflected from a phase conjugation cell, whereas the remaining energy is compressed in Stimulated Brillouin Scattering cells and reflected back with a small time delay. Both methods excite the OPO at the linear stage of amplification from the level of spontaneous noise and provide narrowing of the bandwidth due to many passes of the signal wave through the short length cavity.

PHOTODISSOCIATION DYNAMICS OF WATER MOLECULE AND ITS HYDROGEN-BONDED COMPLEXES IN THE FIRST ABSORPTION BAND

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Ab initio study of the low electronic states S_0 and S_1 of $(H_2O)_n$, $(H_2O...HF)_n$, $(H_2O...HCl)_n$ has been done. It is reported a detailed theoretical study of the $H_2O...H_2O$, $H_2O...HF$ and $H_2O...HCl$ dimers. The ab initio calculations are performed within the ROHF level of theory. The calculations include an ab initio potential surfaces for S_1 states of these complexes and electronic density distributions by the electronic excitation. It is shown that the electronic excitation affects only one water molecule and results in repulsive electronic term. The photodissociation of water in the first absorption band is a prototype system for a fast and direct dissociation process. The total absorption cross section is well known. The formation of such hydrogen-bonded complexes as $(H_2O)_n$, $(H_2O...HF)_n$ and $(H_2O...HCl)_n$ leads to a shift in the absorption band maximum to the blue region with respect to water monomer. The interaction between molecules of complexes results in the broadening of absorption bands. The excited electronic states S_1 found to be characterized an arising from an excitation to a Rydberg orbital.

Invited Lectures N

Friday, September 10, 9:00

Chairman : L. R. BROWN

**SPECTRAL HEADLINES: THE (NON-)APPEARANCE OF
SPECTROSCOPY IN THE MASS MEDIA**

S. MILLER, *Department of Physics and Astronomy, University College
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Many scientists complain that the media does not pay enough attention to science and that when they do, the picture they present is distorted and/or inaccurate. Spectroscopy, in particular, seems to have a pretty thin time of it. So could we do better?

By understanding something of the working of the media themselves – their own rules and priorities – and by learning from experiences – good and bad – scientists can do a lot to help themselves and their cause. This talk will look at one or two examples of spectroscopy that DID make it into the media, and see in what way spectroscopy might better fit in with their requirements.

VIBRONIC COUPLING IN NH_2 AND CH_2 , A PARTNERSHIP OF THEORY AND EXPERIMENT

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Many of the interesting effects in the dynamics of small molecules are associated with a breakdown of the Born-Oppenheimer separation of electronic and nuclear motion, of which the Jahn-Teller and Renner-Teller effects are some of the best known examples. When complex vibronic mixing is caused by the interplay between Renner-Teller and anharmonic coupling in small molecules, the expectation value of the orbital angular momentum, $\langle L_z \rangle$, may be used as a diagnostic of the relative importance of electronic angular momentum and anharmonicity. ^a ^bExamples will be given of the consequences of this for understanding near threshold energy level patterns in CH_2 ,^c the spin-orbit splitting patterns ^d and the structure of the rotationally excited vibronic states of NH_2 .^e

^aG. Duxbury, B. D. McDonald, M. Van Gogh, A. Alijah, Ch. Jungen, and H. Palivan, *J. Chem. Phys.*, **108**, 2336 (1998)

^bG. Duxbury, A. Alijah, B. D. McDonald, and Ch. Jungen, *J. Chem. Phys.*, **108**, 2351 (1998)

^cC. Fockenberg, A. J. Marr, T. J. Sears and B-C. Chan, *J. Mol. Spectrosc.*, **187**, 119 (1998)

^di. Hadj-Bachir, T. R. Huet, J-L. Destombes and M. Vervloet, *J. Mol. Spectrosc.*, **193**, 326 (1999)

^eJ. P. Reid, R. A. Loomis and S. R. Leone, *J. A. C. S. Abstr.* **217**, 169 (1999)

Poster Session O
Friday, September 10, 11:00

ENERGETIC, RADIATIVE AND MAGNETIC PROPERTIES OF THE $i^3\Pi_g^-$ AND $j^3\Delta_g^-$ STATES OF MOLECULAR HYDROGEN IN NONADIABATIC APPROXIMATION

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We present the first successful attempt to calculate energetic, radiative and magnetic properties of the L -uncoupling $i^3\Pi_g^-$ and $j^3\Delta_g^-$ states of molecular hydrogen isotopes in the framework of full *ab initio* nonadiabatic approach. Nonadiabatic rovibronic eigenvalues and wavefunctions (WFs) of the mutually perturbed $i^3\Pi_g^-$ and $j^3\Delta_g^-$ states were derived by direct numerical solution of the two channel-coupling (CC) radial equations. The required electronic L -uncoupling matrix element between $i^3\Pi_g^-$ and $j^3\Delta_g^-$ states as well as $i^3\Pi_g - b^3\Sigma_u^+$, $i^3\Pi_g - e^3\Sigma_u^+$, $i^3\Pi_g - c^3\Pi_u$ and $j^3\Delta_g - c^3\Pi_u$ transition dipole moment functions were estimated from the full configuration interaction (FCI) electronic WFs constructed by a huge GTO basis set while the high-accurate *ab initio* adiabatic potentials for all states under consideration were taken from the literature ^a The theoretical termvalues of both states studied for H_2 and D_2 isotopes agree with their experimental counterparts within 0.5-1.0 cm^{-1} . The remaining discrepancy is attributed to a convergence error of used Born-Oppenheimer curves. The most of calculated magnetic g -factors and branching ratios of the rovibronic transition probabilities to the lower-lying $b^3\Sigma_u^+$, $c^3\Pi_u$ and $e^3\Sigma_u^+$ states coincide with the measured ones within the experimental accuracy. The predicted nonadiabatic transition probabilities remove completely the existing discrepancy between theoretical and accurate experimental lifetimes for $i^3\Pi_g^-$ and $j^3\Delta_g^-$ states ^b

^aW.KOLOS AND J.RYCHLEWSKI, *J.Mol.Spectrosc.***66**, 428 (1977); *ibid* **143**, 237 (1990);
L.WOLNIEWICZ, *J.Mol.Spectrosc.***169**, 329 (1995).

^bM.D.RAY AND G.P.LAFYATIS, *Phys.Rev.Lett.***76**, 2662 (1996).

HYDROGEN BONDING, STRUCTURE AND DYNAMICS OF BENZONITRILE-WATER

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The free jet absorption microwave spectra of the 1:1 complex of benzonitrile with both H₂O and D₂O was investigated to get detailed information on the hydrogen bond and on the dynamics of the large amplitude motion due to the water molecule. The cluster is planar, with the water hydrogen bound to the nitrogen atom of benzonitrile, and the hydrogen bond, far from being linear, is bent so as to form a ring-like structure. A coupled analysis of the 0⁺ and 0⁻ states observed for the normal species was performed and the experimental data were reproduced by a flexible model ^a. The barrier to internal rotation of water was determined to be 287(20) cm⁻¹, considerably lower than the value calculated under assumption of rigidity ^b.

^aR. Meyer, *J. Mol. Spectrosc.* 76, 266 (1979); R. Meyer and W. Caminati, *J. Mol. Spectrosc.* 150, 229 (1991).

^bV. Storm, H. Dreizler, D. Consalvo, *Chem. Phys.* 239, 109 (1997).

MICROWAVE SPECTRUM, INTRAMOLECULAR
HYDROGEN BONDING, CONFORMATIONAL PROPERTIES
AND QUANTUM CHEMICAL CALCULATIONS FOR
3,3,3-TRIFLUOROPROPANOL

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The microwave spectrum of 3,3,3-trifluoropropanol ($\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$) has been investigated in the 7.5 - 60 GHz spectral region at a temperature of approximately -30°C . Five all-staggered rotameric forms are possible for this compound. Two of these conformers denoted **Gg**- and **Aa** were assigned. **Gg**- is stabilised by a six-membered intramolecular hydrogen bond formed between one of the fluorine atoms and the hydrogen atom of the hydroxyl group. No such interaction is possible in **Aa** in which both the O-C-C-C and H-O-C-C chains of atoms is in the anti conformation. The internal hydrogen bond is weak since the **Gg**- rotamer is only $3.5(10) \text{ kJ mol}^{-1}$ more stable than **Aa**. The weak intramolecular hydrogen bond is also evident from the gasphase infrared spectrum of the O-H stretching vibration.

The microwave work has been assisted by *ab initio* computations at the MP2/6-311++G** (frozen core) level of theory, as well as density theory calculations at the B3LYP/6-31G* level. The structural parameters predicted in both these computational schemes are similar. Both methods predict that **Gg**- is several kJ mol^{-1} more stable than other rotameric forms, in agreement with the present experimental findings.

MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF THIIRANE-ARGON AND THIIRANE-NEON VAN DER WAALS COMPLEXES

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The complex thiirane - argon was observed, for the first time, by Lister and Legon.^a They found that the argon atom lies in the C_s symmetry plane of the thiirane molecule. We have recorded the microwave spectra of the ^{34}S , ^{33}S and ^{13}C isotopic species in natural abundance for the complex. The structure determined is close to the structure observed by Lister and Legon. We found a distance $R=3,784 \text{ \AA}$ from the center of mass of thiirane to the argon and an angle $\Theta=100,3^\circ$ between this vector and the bisector of the CSC bond angle of the thiirane molecule.

We have also determined the quadrupole coupling constants for the ^{33}S in the complex and compared them to those determined by H. Dreizler et al.^b for thiirane.

We have also recorded rotational spectra of thiirane- ^{20}Ne and thiirane- ^{22}Ne complexes. Each rotational lines appeared as doublet. We have fitted the mean value frequency of the doublets according to an hamiltonian for a rigid asymmetric molecule. The derived geometric parameters give $R=3,695 \text{ \AA}$ and $\Theta=103,5^\circ$. The doublet shape is attributed to a tunneling internal rotation motion of the thiirane unit within the complex. This effect was already observed by W. Jäger^c for the cyclopropane-Ne complexe.

^aA.C. Legon and D.G. Lister, *Chem. Phys. Lett.* **189**, 149-152 (1992).

^bB. Kirchner, H. Huber, G. Steinebrunner, H. Dreizler, J.U. Grabow and I. Merke, *Z. Naturforsch.* **52a**, 297-305 (1997).

^cY. Xu and W. Jäger, *J. Chem. Phys.* **106**, 7968-7980 (1997).

MICROWAVE SPECTRUM OF THE OPEN-SHELL VAN DER WAALS COMPLEX Ar-ClO₂**MARTIN SCHÄFER and ALFRED BAUDER,***Laboratorium für Physikalische Chemie, ETH Zentrum, CH-8092 Zürich, Switzerland*

Due to its very high resolution, microwave spectroscopy is a very sensitive method, not only for the investigation of molecular geometries, but also for the elucidation of information about the electronic structure through the analysis of the hyperfine structure. In an open-shell van der Waals complex, it is possible to study an eventual perturbation of the electronic structure of the radical upon complexation, or the unpaired electron delocalisation within the complex. But because of the complexity of their rotational spectra, only very few open-shell van der Waals complexes have been studied by microwave spectroscopy.

Chlorine dioxide has been subject of many spectroscopic and photochemical studies because it plays an important role in atmospheric chemistry. There have been some photochemical studies of clusters with ClO₂, but, up to now, no high resolution study of complexes with ClO₂ has been published.

The microwave spectrum of the open-shell complex argon-chlorine dioxide has been measured using a pulsed-jet Fourier transform cavity microwave spectrometer in the frequency range 5–18 GHz. The complex has been formed in a supersonic expansion of ClO₂ entrained in argon. In order to compensate the earth's magnetic field, three pairs of Helmholtz coils have been used. Due to the electron spin-rotation interaction and the hyperfine interaction between the electron spin and the nuclear spin of Cl, all the rotational transitions are split into many lines spread over some 100 MHz. The results of the currently ongoing analysis will be reported.

THE ν_6 AND ν_3 BANDS OF CD_3CN WITH STRONG CORIOLIS INTERACTION AND OTHER PERTURBATIONS

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Methyl cyanide- d_3 molecule has eight fundamental bands. We have earlier investigated them except those two, ν_3 and ν_6 , which are connected to the CD_3 -deformation. These bands have been studied at a resolution of 0.08 cm^{-1} by Matsuura and Murata^a. Their analysis was based on the ν_6 band lines and the Coriolis resonance ν_6/ν_3 without any direct observations for ν_3 . We have now measured the Fourier transform infrared spectrum of CD_3CN in the ν_6/ν_3 -region of $900 - 1230 \text{ cm}^{-1}$ at a resolution of 0.0025 cm^{-1} . The absorption path length was 19.2 m and the sample pressure 0.15 Torr.

The band centre of the strong perpendicular band ν_6 is located at 1046.7 cm^{-1} and the band extends from 901 cm^{-1} to 1175 cm^{-1} . Altogether about 3800 lines were assigned to sub-bands corresponding to $K\Delta K$ values from -19 to +15. The other fundamental, the parallel band ν_3 at 1110.5 cm^{-1} is very weak and it becomes visible only because of the strong Coriolis interaction with ν_6 . Near the crossing region of the resonance about 190 lines could be assigned to three sub-bands $K = 8 - 10$ of ν_3 . The effects of the Coriolis resonance in ν_6 are strikingly visible near the crossing. The Q branch RQ_9 is degrading strongly downwards in wavenumbers and ${}^RQ_{10}$ upwards, the largest shifts being of the order of 10 cm^{-1} . In addition the ℓ -doubling in RQ_0 is really gigantic. In the analysis the main interaction to be taken into account is naturally this Coriolis resonance ν_6/ν_3 . There is also an $\ell(1,-2)$ resonance between these fundamentals. Many resonances with other vibrational levels must also be considered. The second overtone $3\nu_8$ of the lowest fundamental perturbs ν_6 through an anharmonic resonance and several different perturbations are due to the combinations $\nu_4 + \nu_8$ and $\nu_7 + \nu_8$.

^a H. Matsuura and H. Murata *Bull. Chem. Soc. Jpn.* **55**, 3129-3134 (1982)

THE N-N INFRARED BAND OF HYDRAZINE

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The analysis of a high resolution infrared spectrum of hydrazine in the 729 - 1198 cm^{-1} region, recorded at the University of Paris, revealed, in addition to two earlier assigned inversion bands, the existence of another fundamental in the upper part of the spectrum. This band could be assigned as the ν_3 N-N stretching band of hydrazine. The assignment was based on the ab initio calculation and the force constant study by Giguere and Liu ^a.

In the paper the analysis of the rovibrational states up to $K'=6$ is presented. A total number of 1500 lines have been assigned. The band is only weakly perturbed. The band center is located at 1077.2416 cm^{-1} . The inversion splitting is about 4.8 cm^{-1} compared to 0.5 cm^{-1} in the ground state and 13.7 cm^{-1} in the antisymmetric inversion state. The $(B+C)/2$ constant of 23897 MHz is slightly smaller than that for the ground state of 24076 MHz which should be expected for a N-N stretching vibration. The band was fitted using the effective group-theoretical Hamiltonian.

^a *J. Chem. Phys.* **20**, 136-140 (1952)

MILLIMETER-WAVE STUDY OF CH_3SiD_3 IN THE
($v_6 = 0, 1, 2, 3$) and ($v_{12} = 1$) STATES

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Pure rotational spectra of CH_3SiD_3 in the ($v_6 = 0, 1, 2, 3$) and ($v_{12} = 1$) states were observed in the region from 152 to 308 GHz using millimeter-wave spectroscopy. Here v_{12} and v_6 are, respectively, the principal quantum numbers for the silyl rocking mode and for the torsion between the silyl and methyl groups. More than 450 rotational frequencies were measured with $J = 7, 11, \text{ and } 15$. These new measurements were combined with more than 4400 infrared measurements for the ($v_6 = 2 \leftarrow 0$), ($v_6 = 3 \leftarrow 1$) and ($v_{12} = 1 \leftarrow 0$) bands and fitted simultaneously in a two-band model that consists of the torsional stack of levels ($v_6 = 0, 1, 2, 3, \dots$) in the ground vibrational state and that in the ($v_{12} = 1$) state. The aim of this study is to investigate rotation-torsion-vibration interactions that occur between torsional states close to the free rotor limit and small amplitude vibrational motion. The leading Hamiltonian terms off-diagonal in vibrational quantum are of xy-Coriolis type. In this case, the near degeneracy occurs between the ($v_6 = 3, v_{12} = 0$) and ($v_6 = 0, v_{12} = 1, \ell_{12} = +1$) states introducing a typical shift of 100 MHz in the rotational line positions. The structure of the Hamiltonian and the values for the molecular parameters are in a good agreement with the results obtained for the protonated methyl silane CH_3SiH_3 ^a.

^aN. Moazzen-Ahmadi, I. Ozier, G. A. McRae, and E. A. Cohen, *J. Mol. Spectrosc.*, **175**, 54-61 (1996)

THE ROTATIONAL SPECTRUM OF BiO IN ITS $X_1^2\Pi_{1/2}$ AND $X_2^2\Pi_{3/2}$ ELECTRONIC STATES

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BiO has a $^2\Pi_r$ electronic ground state with a fine structure interval of $\approx 7087 \text{ cm}^{-1}$ between the X_1 and X_2 states. A recent, far reaching study of the BiO radical by Shestakov, *et al.*,^a has provided spectroscopic constants for a total of nine of its electronic states. The rotational constants calculated for the $X^2\Pi$ state have been used as the basis for a further investigation by microwave spectroscopy at Nobeyama Radio Observatory. BiO was produced in a flow system by heating Bi to 1120 K in a Knudsen cell and reacting the resulting vapor with an approximately 1:1 mixture of O_2 and argon in the presence of a dc discharge. A useful side-effect of this method of production is the population of highly excited vibrational states of BiO. This is presumably due to collisional energy transfer from the metastable $a^1\Delta_g$ electronic state of O_2 . As a result, rotational transitions within vibrationally excited levels up to $v < 9$ in the $X_1^2\Pi_{1/2}$ electronic state and $v < 5$ in the $X_2^2\Pi_{3/2}$ state have been observed. A sample microwave spectrum of the BiO radical is given in Figure 1, which illustrates the hyperfine pattern that is associated with the presence of the $I < 9/2$ ^{209}Bi nucleus.

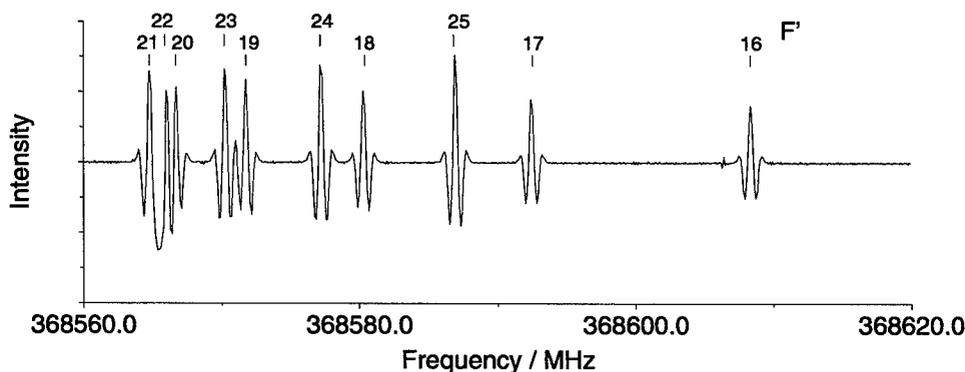


Figure 1: The BiO $X_1^2\Pi_{1/2}$ ($v = 0$) $\Delta F = +1$, $J = 41/2 - 39/2$ transitions.

^aO. Shestakov, R. Breidohr, H. Demes, K. D. Setzer and E. H. Fink *J. Mol. Spectrosc.* **190**, 28-77 (1998)

Thus far, a total of 575 lines have been assigned and fitted with an RMS of 27 kHz, using an effective Hamiltonian similar to that of Brown *et al.*^b There is excellent agreement between the microwave parameters and those obtained in the optical study. More recently, we have included over 2300 previously assigned transitions of the $X_2 \rightarrow X_1$ 0-0 emission band^c with an RMS of 0.0009 cm^{-1} . In addition, the hyperfine parameters for both the X_1 and X_2 electronic states have been determined. These will be compared to the corresponding parameters of related compounds and to those of the bismuth atom.

^bJ. M. Brown, E. A. Colbourn, J. K. G. Watson and F. D. Wayne, *J. Mol. Spectrosc.* **74**, 294-318 (1979)

^cE. H. Fink, private communication

**ANALYSIS OF THE ν_2 FUNDAMENTAL OF D_2CO WITH
FERMI-TYPE INTERACTION $\nu_2/2\nu_4$** **JARMO LOHILATHI, SEPPÖ ALANKO, MATTI****KOIVUSAARI**, *Department of Physical Sciences, University of Oulu, P.O.
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High resolution Fourier transform infrared spectra the $\nu_2(A_1)$ band of D_2CO molecule have been recorded in Oulu. The band lies in the wavenumber region 1590-1770 cm^{-1} and the band centre is at 1701,62 cm^{-1} . Instrumental resolution, 0,004 cm^{-1} , was chosen according to the Doppler line width of the molecule at this region (about 0,0037 cm^{-1}). Different absorption conditions were needed because of the intensity differences between strong and very weak lines: for the path length 3,2 m pressures were 0,0018, 0,17 and 1,8 Torr and for 32 m it was 1,8 Torr.

The selection rules for the band are $\Delta J = 0, \pm 1$, $\Delta K_a = 0, \pm 2$ and $\Delta K_c = \pm 1$, i.e. the transitions are of a-type and the spectrum resembles that of a parallel band of a symmetric top. More than 1700 rotation vibrational lines have been assigned up to $J = 50$ and $K_a = 17$. In this analysis J and K_a reach larger values than in the previous analysis^a and some transitions of the type $\Delta K_a = \pm 2$, $\Delta K_c = \pm 1$, which are very weak, have also been detected and included in the present analysis.

The ν_2 band is perturbed by the Fermi interaction with $2\nu_4(A_1)$ (band centre at 1867 cm^{-1}) as mentioned in the previous study^b. However, this resonance has not been taken into account in the earlier analysis. Some lines of the $2\nu_4$ band have been assigned for the first time and will be presented. They have been used to explain the resonance perturbation in the ν_2 band. The assigned transitions of the ν_2 band were fitted to the Watson-type rotational Hamiltonian using I^r representation in both A- and S-reduction.

^aS. TATEMATSU, T. NAKAGAWA, K. KUCHITSU, J. OVEREND, *Spectrochim. Acta*, vol. 30A 1585-1604 (1974)

^bS.-C. HSU, R. H. SCHWENDEMAN, G. MAGERL, *J. Molec. Spectrosc.*, vol. 136, 157-168 (1989)

THE MICROWAVE AND MM-WAVE SPECTRUM OF THE
GROUND AND ONE TORSIONAL EXCITED STATE OF
ACETONE

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An effective rotational Hamiltonian for molecules with two periodic large-amplitude motions^a has been used to analyze the rotational spectrum of acetone, CH₃COCH₃. For the analysis of the vibrational ground state, microwave and mm-wave data from the literature were combined with new measurements between 260 and 610 GHz in a global fit of all four torsional substates. Over 600 transition frequencies involving energy levels with J up to 60 were fit with 38 spectroscopic parameters to about two times the experimental precision. The following parameters were determined in the least-squares fit: $\rho = 0.0622373(92)$, $\beta = 25.976(12)$ deg., parameters equivalent to the rotational, quartic and sextic distortion constants, the internal energy tunneling parameters (among them $\epsilon_{01} = -763.499(103)$ MHz) and tunneling constants related to the rotational and distortion constants. The rotational spectrum of a torsional excited state was assigned between 260 and 350 GHz. In a preliminary least-squares fit, over 200 transition frequencies from all four torsional substates were fit with the effective rotational Hamiltonian with 20 variable parameters. The leading term of the tunneling energy, ϵ_{01} was with 5702(15) MHz about eight times larger than in the ground state.

^aP. Groner *J. Chem. Phys.* **107**, 4483 (1997).

HIGH RESOLUTION ANALYSIS OF H₂CO IN THE 3.6 AND 4.3 μ m REGION BY FOURIER TRANSFORM SPECTROSCOPY

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The analysis of the 4 μ m bands of formaldehyde was undertaken because this spectral region is currently used for the detection of this molecule in the troposphere. Using new Fourier transform spectra recorded at high resolution at LPMA in Paris, it has been possible to perform an extensive study of the formaldehyde absorption spectra in the 2600-3000cm⁻¹ and in the 2200-2500cm⁻¹ spectral ranges. This analysis was started using the results obtained previously in the same spectral regions ^{a,b} and by using the ground state parameters of Bocquet et al ^c In this way, more than 9000 lines were identified which belong to 10 bands of formaldehyde. From this analysis it appears that these these bands should not be considered as independent.

Actually in the high frequency range, the analysis of the strongest bands, namely ν_1 and ν_5 (symmetric and antisymmetric stretching modes) was complicated by the existence of Fermi-type resonances and by A-type, B-type and C-type Coriolis interactions with various overtone or combination states namely $\nu_2 + \nu_6$, $2\nu_3$, $\nu_2 + \nu_4$, $\nu_3 + \nu_6$ and $\nu_3 + \nu_4$.

Moreover the analysis was also complicated by additional perturbations due to the weak $2\nu_4$ and $2\nu_6$ bands and to the very weak $\nu_4 + \nu_6$ band which appear in the low frequency range. The final calculation which involves about 2600 levels belonging to 10 different states leads to rather reasonable results, given the difficulty of the problem.

^aL. R. Brown, R. H. Hunt, and A. Pine, *J. Mol. Spectrosc.* **75**, 406 (1979).

^bF. Ito, T. Nakanaga, and H. Takeo, *Spectrochimica Acta.* **50A**, 1397 (1994).

^cR. Bocquet, J. Demaison, L. Poteau, M. Liedtke, S. Belov, K.M.T. Yamada, G. Winnewisser, C. Gerke, J. Grip and Th. Kohler, *J. Mol. Spectrosc.* **177**, 154 (1996) and J. Demaison (private communication)

STUDY OF THE INFRARED ABSORPTION SPECTRUM OF SF₆ NEAR 950 cm⁻¹

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Sulfur hexafluoride appears to be a species of growing importance in the field of atmospheric physics and chemistry since it is now recognized as a pollutant that can contribute to the greenhouse effect. SF₆ concentration in Earth's atmosphere is presently small but increases at a rate of around 8 % per year due to industrial rejections.

The strongest absorption region in the SF₆ infrared spectrum lies around 950 cm⁻¹ and is of particular interest because *i*) this is the main region that contributes to the greenhouse capabilities of this molecule and *ii*) it is used to monitor the SF₆ concentration in the atmosphere. It is therefore necessary to obtain accurate models of this absorption.

The 950 cm⁻¹ region is mostly dominated by the very strong ν_3 stretching fundamental. However, at $T = 300$ K the hot bands (mainly $\nu_3 + \nu_6 - \nu_6$) contribute for more than 30% of the absorption. Such hot bands had never been studied in detail up to now (as a matter of fact, apart for ν_3 itself, there exist only a very few high resolution studies concerning SF₆^a).

Using the LADIR's Fourier Transform Spectrometer we could measure quite easily the hot band absorption. The spectra recorded in Lille with a sideband spectrometer are used to assign octahedral structures.

The intensity of the ν_3 spectrum has been studied in Dijon using the results of the frequency analysis of this band^b. Calculations were realized using the STDS software^c. A first estimation of the ν_3 dipole moment parameter $\mu_{0,3}$ has been obtained. These values were used to calculate the $\nu_3 + \nu_6 - \nu_6$ hot band

^aV. Boudon, M. Hepp, M. Herman, I. Pak and G. Pierre, *J. Mol. Spectrosc.*, **192**, 359–367 (1998).

^bO. Acef, Ch. J. Bordé, A. Clairon, G. Pierre and B. Sartakow, *to be published*.

^cCh. Wenger, V. Boudon, J.-P. Champion and G. Pierre, *to be published*.

spectrum. The positions of the four sublevels of $\nu_3 + \nu_6$ could be estimated and will be presented in this poster.

Others hot bands like $\nu_3 + \nu_5 - \nu_5$ not studied up to now can be observed in the experimental spectra and can give some informations on both $\nu_3 + \nu_5$ and ν_5 vibrational levels.

STUDY OF THE FUNDAMENTAL BANDS OF $^{70}\text{GeD}_4$ BY RAMAN AND INFRARED SPECTROSCOPY

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The 4 fundamental bands of $^{70}\text{GeD}_4$ have been investigated out using a Hamiltonian build up by coupling of irreducible tensors in the T_d group. Both infrared and Raman spectra are used to observe all fundamental bands.

Infrared spectra of monoisotopic $^{70}\text{GeD}_4$ were recorded in the 600 cm^{-1} and in the 1500 cm^{-1} region using the Bruker 120HR interferometer at Wuppertal. The resolution (1 / maximum optical path difference) was between 2.3 and $3.3 \times 10^{-3}\text{ cm}^{-1}$ in order to observe the active infrared fundamental bands ν_3 and ν_4 and the interacting ν_2 band. A high resolution Raman spectrum of ν_1 band $^{70}\text{GeD}_4$ molecule has been recorded and analyzed. The recording has been made using a high resolution spectrometer based on the inverse Raman effect.

The analysis was performed using a modified version of the STDS (Spherical Top Data System) software developed in Dijon.

The bending modes ν_2 and ν_4 are in interaction and have been treated as a dyad. More than 1100 lines have been assigned and fitted using the 6th order of development of the Hamiltonian. The standard deviation obtained for these lines is about $5.3 \times 10^{-3}\text{ cm}^{-1}$.

The stretching modes ν_1 and ν_3 are also in weak interaction and are hence also treated together. More than 600 infrared lines of ν_3 and about 80 Raman lines of ν_1 have been analysed using the 5th order of development of the Hamiltonian. The standard deviation obtained for these two groups of lines is $4.7 \times 10^{-3}\text{ cm}^{-1}$ for infrared lines and $1.8 \times 10^{-3}\text{ cm}^{-1}$ for Raman lines, respectively.

The ground state is developed up to the 6th order and the values of its parameters are common to the two dyads.

**APPARENT PRESSURE SHIFT OF ROTATIONAL
TRANSITIONS AS A CONSEQUENCE OF THE INTERNAL
STRUCTURE OF LEVELS**

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Pressure dependent shift of peak position and line asymmetry is discussed for the cases of unresolved hyperfine structures of rotational levels. This asymmetry depends on line widths of the spectral components, the magnitude of the hyperfine splitting and rotational quantum numbers. With the increasing line widths of the individual fine components, the frequency shift and the line asymmetry vanishes. This line shift effect is only apparent and its wrong diagnose can unfavorably affect measurements of the real pressure shift as well as the calibration of FIR FT spectra. The effect is demonstrated on ammonia and acetonitrile rotation transitions.

NEW FEATURES OF THE MOGADOC DATABASE (MOLECULAR GASPHASE DOCUMENTATION)

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The MOGADOC database (Molecular Gasphase Documentation) deals with compounds which have been studied in the gasphase by means of electron diffraction, microwave spectroscopy or radio astronomy. Presently the database contains over 25,700 bibliographic references for about 7,600 inorganic, organic and organometallic compounds including numerical datasets for bond lengths and angles for about 4,000 compounds.

Search Field	Operator	Criteria	Hits
Global Search		?FLUBRO? AND STRU?TUR??	548
Accession Number	AND		
Author(s)	AND	KUCZKOWSKI, R L OR FRASER, ?	377
Source	AND		
Journal Code	AND		
Publication Year	AND	>=1990	9967
Document Type	AND	JOURNAL	25592
Molecular Formula	AND		
Editor(s)	OR		
	NOT		
Keywords	AND	FOURIERMETHOD	1433
Language	AND		
Suppl. Terms	AND		
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Tabular query form for the bibliographic file of MOGADOC with a retrieval example.

The WindowsTM version of this valuable retrieval tool with its user-friendly graphical input interfaces and additional retrieval features is described.

The following new retrieval features

- extensive interactive thesaurus functions
 - fuzzy search
 - statistical functions
- will be demonstrated.

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COLLISIONAL COOLING: A ROUTE TO DETERMINING KEY PROPERTIES OF HYDROFLUOROCARBON VAPOURS RELEVANT TO GLOBAL WARMING

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We have obtained high-resolution infra-red spectra of C_2F_6 , C_4F_8 , and CF_3CFH_2 at 300K, 200K, and 77K, and are in the process of analysing various vibration-rotation bands in each. The gases are replacement Hydrofluorocarbon gases and as such precise knowledge of their absorptions and molecular constants is essential for greenhouse effect calculations such as radiative forcing. The room temperature and 200K measurements have been taken using the Bomem DA FTIR spectrometer at Strathclyde University and the Bruker spectrometer at RAL, and the 77K measurements have been obtained at RAL using the method of collisional cooling there developed.^a Collisional cooling greatly simplifies the spectra by eliminating many of the hot bands. Previous work on these gases includes that of Hansford & Davies,^b Newnham et al,^c Nakanaga et al,^d McNaughton et al,^e and Xu et al.^f In our current presentation we will concentrate on the analysis of the 'immortal' molecule C_2F_6 . Eventually we intend to model the vibrational-rotational behaviour of each gas with respect to temperature.

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^bG. M. Hansford & P. B. Davies, *J. Mol. Spec.* 180 (1996)

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^dTaisuke Nakanaga, Fumiyuki Ito, Jun Miyawaki, Ko-ichi Sugawara, Harutoshi Takeo, Atsuo Suga, *J. Mol. Spec* 178 40-44 (1996)

^eDon McNaughton, Corey Evans, Evan G Robertson *Chem. Soc. Faraday Trans.* 91(12)1723-28 (1995)

^fLi-Hong Xu, Anne M. Andrews, Richard R. Cavanagh, Gerald T. Fraser, Karl K. Irikura, Frank J. Lovas *J. Phys. Chem. A* 101 2288-2297 (1997)

TORSIONAL SPLITTINGS OF ^{70}Ge -DIGERMANE IN THE DEGENERATE VIBRATIONAL STATES

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It is shown that the torsional splitting of ethane-like molecules in the degenerate vibrational states depends on the value of the Coriolis ζ -coefficient. The splitting is predicted to reach the maximum value for ζ close to one (pure E_{1d} or E_{2d} vibrational states), decreasing as the value of ζ decreases. Such behavior is determined by the combined effects of torsional Coriolis interactions and end-to-end coupling.

The detailed rotational-torsional analysis of the $\nu_6(A_1)$ and $\nu_8(E_u)$ fundamentals of the ^{70}Ge -Digermane shows torsional splittings of 0.049 cm^{-1} in both ground state and ν_6 state. The splitting decreases almost to zero in the degenerate ν_8 state, with $\zeta = -0.31$. The torsional splittings observed in the other two infrared active degenerate fundamentals, ν_7 with $\zeta = -0.04$ and ν_9 with $\zeta = 0.25$, follow the expected trend.

Explorative numerical calculations confirm that the proposed mechanisms can explain the experimental results.

DETECTION OF NO BY LASER MAGNETIC RESONANCE

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Nitric oxide is made responsible for environmental pollution but on the other hand it is also produced in the human body. There it takes part in many physiological and pathophysiological mechanisms, for example the regulation of the diameter of blood vessels.

The characteristics of our LMR-spectrometer (eg low detection limit and high resolution in the time domain) facilitate the detection of NO which is produced in the respiratory tract. Using the LMR spectrometer it is possible to get information about the release of nitric oxide in the lower and upper respiratory tract and even about the dynamics of NO in the paranasal sinuses.

Under physiological conditions NO is only stable for some seconds. With the LMR-spectrometer we can also measure low concentrations of nitrite ions which are produced after the reaction of nitric oxide with oxygen. The experimental setup and some examples of measurements are given which demonstrate the advantages of this technique.

THE IR-SPECTRUM OF DICYANOACETYLENE BETWEEN 1950 AND 3600 cm^{-1}

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In continuation of earlier studies^a of the molecule NC-CC-CN, we have investigated the many combination band systems in the region above 1950 cm^{-1} in detail. Several hot bands from the $v_9 = 1, 2,$ and 3 states have been identified. In agreement with expectation most bands are disturbed by local anharmonic resonances.

Of the three stretching fundamentals $\nu_1, \nu_2,$ and ν_4 only the latter is IR-active in dicyanoacetylene, whereas for the closely analogous iso-compound NC-CC-NC all three bands have been observed^b. Comparisons of the hot band systems of the two molecules shall be presented.

^aF. Winther, P. Warmann, M. Schönhoff, and H. Mäder, *J. Mol. Struct.*, in press.

^bC. Bartel et al., *Angew. Chem.*(1998), 110, 3036

COMPARISON BETWEEN QUANTUM COUPLED STATES
AND SEMICLASSICAL CALCULATIONS OF $Q(J)$ ($J = 0, 1, 2$)
LINE SHAPE PARAMETERS IN PURE HYDROGEN

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The self perturbed hydrogen spectrum is often used as a probe for temperature measurements in combustion media, for example hydrogen CARS Thermometry[1] in hydrogen-oxygen flames. The purpose of this work is to determine collisional broadening and shifting coefficients of $Q(J)$ ($J = 0, 1, 2$) lines using the quantum coupled states (CS) method and the so called Robert-Bonamy (RB) semiclassical approach[2]. Since quantum calculations are not possible in the range of combustion temperature (2000K-3000K), the semiclassical method is tested in the 50-500K temperature range where CS calculations are performed with the MOLSCAT [3] code using an analytical potential energy surface (PES). This PES is useful in the RB semiclassical calculations since it leads to analytical expressions of the different contributions to the broadening and shifting coefficients. The PES is written as a sum of electrostatic and atom-atom contributions. The comparison between CS and RB calculations will improve our knowledge of the validity of the semiclassical approximation for a typical quantum system such as self perturbed hydrogen. A comparison with experimental data will allow us to test the accuracy of this PES.

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TEMPERATURE DEPENDENCE OF LINE BROADENING
AND LINE SHIFTING IN PURE ROTATIONAL S_0 AND
VIBRATIONAL Q BRANCHES OF H_2 IN H_2O

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For years, hydrogen has been used as a probe molecule for CARS thermometry in $H_2 - O_2$ cryogenic combustion at high pressure. As water is a product of the combustion, the contributions of $H_2 - H_2$ and $H_2 - H_2O$ collisions to the line broadening and line shifting are needed to determine the temperature.

Collisional parameters of the $S_0(J = 0-4)$ and $Q(J = 0-7)$ lines obtained in $H_2 - H_2O$ mixtures between 596 and 1200K are presented. The linewidths and the line shifts vary linearly versus water concentration and no asymmetry of the spectral lines was observed in the collisional regime. Then no evidence of speed effect appears in the case of H_2 perturbed by water; contrary to other heavy perturbers studied previously [1-3]. At each temperature, it was then possible to extract the $H_2 - H_2O$ contributions through the usual "mixing rule".

The experimental results show singular behavior with the temperature. While the broadening coefficients in the Q branch increase monotonically versus temperature, they first increase up to 1000K and then dramatically decrease at higher temperature in the pure rotational S_0 branch. Moreover, the Q branch shifting coefficients decrease monotonically with temperature; which had never been observed before in the analysis of the spectral line shape of H_2 with other perturbers [4]. In the pure rotational S_0 branch, the dependence of the shifting coefficients is erratic contrary to $H_2 - H_2$ and $H_2 - He$ collisional systems [5].

While semi-classical calculations are in relatively good agreement concerning the $Q(J)$ lines broadening, they cannot reproduce the singularities observed. Further developments are now in work concerning the convergence of the atom-atom potential and the availability of the second order development of the S matrix for this particular system.

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WATER VAPOR LINE SHIFTING OF THE $\nu_1 + \nu_2$ END $\nu_2 + \nu_3$ BANDS INDUCED BY O_2 AND Ar PRESSURE

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Measurements and calculations of the oxygen and argon pressure - induced shift coefficients for more than 100 water vapor absorption lines of the (011)-(000) and (011)-(000) bands have been performed. Experimental data on line shift coefficients were obtained from the analysis of $H_2O - O_2$, Ar room temperature absorption spectra at 11 different pressures of O_2 over the range from 148.5 Torr to 3800.4 Torr, using a Fourier transform spectrometer with spectral resolution of 0.007 cm^{-1} and an optical pathlength of 84.05 m. To study the details of O_2 and Ar shifting the Anderson semiclassical impact theory was used in the calculations of line shift coefficients. This method allows to account for the contributions from different interactions separately. In the case of $H_2O - O_2$ collisions the main contribution to broadening and shifting is due to interaction between dipole moment of water and quadrupole moment of oxygen. We have also included the quadrupole-quadrupole, induction and dispersion terms into consideration. For the $H_2O - Ar$ system the induction and dispersion terms of the polarisation potential are only important. In spite of the facts that the different interactions are essential for $H_2O - O_2$ and $H_2O - Ar$ collisions the trends of shifting for them are similar. The calculated results are compared with measurements and good agreement is observed. The rotational dependence of the line shifts is discussed. The authors acknowledge the support by the Russian Foundation of Fundamental Research (Grants N 98-02-16375 and N 98-02-17772).

**BROADENING AND SHIFT BY COLLISIONS WITH ARGON
FOR HCO⁺ ROTATIONAL LINES**

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Different methods of calculations are compared to experiments at 77 K for the broadening Γ and shift s of some HCO⁺ rotational transitions by collisions with Argon. Capture method and Anderson, Tsao and Curnutte (ATC) method with straight line trajectories are both not able to reproduce the trend of Γ with J . A discussion of the origin of such a discrepancy allows us to obtain better insights into the different causes of collisional relaxation for the rotational state of molecular ions. Quite good agreement is obtained both by the hybrid method proposed by Liao and Herbst or by ATC calculations using a more realistic translational dynamics. However, some discrepancy still exists for high J values. The possible reasons of this are briefly discussed.

**THE INFRARED SPECTRUM OF CH₃D
BETWEEN 900 AND 3200 cm⁻¹**

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The high resolution infrared spectrum of CH₃D in the region from 900 to 3200 cm⁻¹ was analysed on the basis of Fourier Transform spectra recorded at Kitt Peak and at Giessen. A theoretical model for an effective hamiltonian in terms of irreducible tensor operators recently adapted to symmetric top molecules was used in order to consider simultaneously all available transitions between the lowest three polyads of the molecule: the Ground State (G.S.), the Triad (3 interacting fundamental bands in the 8 μm region) and the Nonad (9 interacting bands in the 4 μm region). The effective Hamiltonian for the Triad and Nonad systems contains 257 parameters from a set of 1609 symmetry allowed terms through the sixth order of approximation. A simultaneous fit of 3467 Triad–G.S., 5590 Nonad–G.S., and 2323 Nonad–Triad (hot band) transition wavenumbers were done. The standard deviations achieved were respectively 2 10⁻³ cm⁻¹ for the positions and 4.3 % for the intensities. This accuracy is very similar to that obtained for the tetrahedral species of methane. The overall result of recent efforts is that the methane transitions at room temperature are modeled with a precision close to the precision required for the remote sensing of atmospheres.

ROTATIONAL DEPENDENCE OF GIANT l -DOUBLING IN SYMMETRIC TOP MOLECULES

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The first order Coriolis resonance between nondegenerate ν_s and degenerate ν_t fundamentals in symmetric top molecules give rise to the doubling of the sublevels of mode ν_t with values of quantum number $k = l = 1$ of the projection on the symmetry axis of full and vibrational moment degenerate mode. In dominant approximation the energy splitting depend linearly on the quantum member of full angular momentum J . Effective Hamiltonian for giant l -doubling in symmetric top molecules has been developed on the base of theory of linked ordering schemes of rovibrational interactions developed by one from authors (VMM). Theory of non-linear sequence transformation is applied for the analysis of arising approximate series on J^2 . Diagonal Pade approximants for rovibrational dependence of giant l -doubling can be presented in the form:

$$\tilde{H}_{giant\ doubling} = \sum \tau a_t^{\sigma\tau} J_\tau \alpha \left\{ 1 + \frac{C_{2,J}^2}{C_{2,J} - C_{4,J}J^2} J^2 + \dots \right\}$$

where α , $C_{2,J}$ and $C_{4,J}$ are coefficients in operators H_{21} , H_{23} and H_{25} correspondingly, $a_t^{\sigma\tau}$, $J_{-\tau}$, J^2 are generally accepted vibrational and rotational ladder operators.

ROTATIONAL ANALYSIS OF THE NEAR INFRARED SINGLET-TRIPLET ELECTRONIC SPECTRUM OF OZONE

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High Resolution Fourier Transform Infrared Spectrometry was used to study the rotational fine structure of the singlet-triplet electronic spectra of ozone $^{16}\text{O}_3$ and $^{18}\text{O}_3$ in the range $9300\text{-}10200\text{ cm}^{-1}$. With a near pure case (b) coupling model, we succeeded to assign 4 sets of lines for two rovibrational bands of each isotopomer. A combined least-squares/ band contour analysis yielded an overall standard deviation of the order of $0.025\text{-}0.045\text{ cm}^{-1}$. The rotational analysis has established that the upper state is $^3\text{A}_2$ in agreement with recent theoretical calculations. Numerous perturbations are observed in the spectra of both isotopomers and limited our least-squares fit to the three rotational constants, the symmetric top distortion constants and the alpha and beta spin spin constants. The existence of perturbations in the first vibrational levels of the $^3\text{A}_2$ state is justified by several level-crossings with high vibrational levels of the ground state.

THE $A^2\Pi - X^2\Sigma^+$ SYSTEM OF THE LaO MOLECULE

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The $A^2\Pi - X^2\Sigma^+$ system of LaO, excited in the discharge of a hollow-cathode lamp, has been recorded by Fourier transform spectroscopy, at a resolution of 0.050 cm^{-1} , in the spectral region from 12300 to 13550 cm^{-1} (subsystems $^2\Pi_{1/2} - X^2\Sigma^+$ and $^2\Pi_{3/2} - X^2\Sigma^+$). The first six bands of the $\Delta v=0$ sequence are observed. A thorough analysis of the line intensities and FWHM in the 16 branches of the 0-0 band is carried out. A rotational temperature of about 600 K is derived. Linewidths and their evolution with rotation in each branch are well interpreted in a semiquantitative approach. A consistent set of effective spectroscopic constants for both electronic states is obtained ($A^2\Pi(v' = 0 - 5)$ and $X^2\Sigma^+(v'' = 0 - 5)$), from the global processing of the wavenumbers of some 1200 lines in the six bands. Line lists are available, which are expected to be useful for high resolution syntheses of S-type stellar spectra.

A DIATOMIC POLAR AND POLARISABLE MOLECULE IN AN ELECTRIC FIELD

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The Schrodinger equation describing a diatomic molecule having a permanent dipole moment and a static dipolar polarizability, modeled by a linear rigid rotor, in an electric field is similar to that for the movement of an electron in the field of two infinitively heavy nuclei. By expanding the wavefunctions on the basis of spherical harmonics, the resolution process is reduced to the diagonalization of a symmetric pentadiagonal matrix. Eigenenergies and eigenfunctions are obtainable in that simple way with any desired accuracy for any states. Exact derivatives of the eigenenergies with respect to the electric field, related to the deflection of a molecular beam in an inhomogenous electric field from which dipole and polarizability are experimentally determined, are also obtained. From the eigenfunctions, the distribution probability of the polar angle between the molecular axis and the electric field can be evaluated exactly and compared to usual expansions in terms of Legendre polynomials. Results will be presented for LiNa experimentally investigated in our Laboratory and for LiK which is by far more polar than LiNa.

SINGLET STATES OF K₂ CORRELATING WITH THE K(4s)+K(4p) ASYMPTOTE

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Infrared fluorescence from the potassium dimer has been recorded by Fourier transform spectrometry following excitation of the C ¹Π_u state using a cw tunable dye laser emitting around 430 nm. Transitions to two electronic states are observed between 6000 and 10000 cm⁻¹. The stronger of the two is the C ¹Π_u - 1 ¹Π_g system, which dominates the spectra from 6000 - 9000 cm⁻¹. Levels up to v = 107 in the 1 ¹Π_g state are observed, describing the potential curve for this state out to 40 Å^a. The weaker system corresponds to C ¹Π_u - 2 ¹Σ_g⁺ transitions, for which the Franck-Condon factors are rather more restrictive. Levels 0 ≤ v'' ≤ 30 in the 2 ¹Σ_g⁺ state are observed, covering only 30 % of the potential well^b. This is the first observation of the 2 ¹Σ_g⁺ state in K₂, which has T_e = 14342.69(9)cm⁻¹, ω_e = 47.965(9)cm⁻¹ and B_e = 0.03300(4) cm⁻¹.

Vibrational levels 89 ≤ v'' ≤ 127 of the 1 ¹Π_g state have also been observed at very high resolution in photoassociation experiments performed in Connecticut^c, supplying accurate binding energies for J < 3 in these levels. Combining data from photoassociation and fluorescence experiments, we have constructed a potential curve for the 1 ¹Π_g state which extends to 60 Å, from which reliable long-range parameters governing the K(4s) + K(4p) interaction have been derived using an asymptotic treatment of the Coulombic and exchange terms in a Hund's case c) basis. The parameters derived from a fit of the 1 ¹Π_g potential curve from 9 to 60 Å can then be used to calculate the unobserved part of the 2 ¹Σ_g⁺ state. This predicts a barrier to dissociation of 295 cm⁻¹ in the 2 ¹Σ_g⁺ state located at 9.08 Å, significantly lower in energy and at longer internuclear distance, than predicted by recent pseudopotential + C.I. calculations.^d

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^dS. Magnier and P. Millié, in Phys. Rev. A 54 204-218 (1996)

HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CHLORYL FLUORIDE, FCIO_2

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High resolution infrared spectra of the very asymmetric, oblate top ($\kappa = 0.4108$ for $\text{F}^{35}\text{ClO}_2$) have been recorded and analyzed for the first time. The spectra are congested due to the presence of two major isotopic species, $\text{F}^{35}\text{ClO}_2$ (75.41 %) and $\text{F}^{37}\text{ClO}_2$ (24.11 %), as well as several hot bands.

Based on ground state spectroscopic constants recently improved and new matrix IR data,^a it was possible to analyze the A' ν_2 and ν_3 bands for both isotopomers. These bands, centered at 630.432 and 547.560 cm^{-1} , respectively, for $\text{F}^{35}\text{ClO}_2$, are predominantly a type in character. Even though the levels can be treated as isolated states, a more satisfactory fit is obtained if the first order Coriolis interaction between these two states, determined from the harmonic force field,^a is taken into account.

After these analyses have been essentially completed, and simultaneously with the investigations of the A' ν_4 and A'' ν_6 bands, pure rotational transitions have been identified for all of the four respective vibrational state in the microwave and submillimeter wave regions.

The analyses of the ν_4 and the purely b type ν_6 bands, centered at 405.716 and 358.839 cm^{-1} , respectively, for $\text{F}^{35}\text{ClO}_2$, are presently under way. The Coriolis interaction between ν_4 and ν_6 is more pronounced than between ν_2 and ν_3 since the energy difference is smaller, and furthermore, the respective interaction constants are fairly large.

^aH. S. P. Müller, *J. Mol. Struct.*, in press

ABSORPTION AND EMISSION SPECTROSCOPY OF YTTERBIUM IN SOLID ARGON

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This progress report covers an important part of the ongoing study on cluster and complex formation of all *f*-block metal atoms at the matrix laboratory in Mülheim. Ytterbium offers an excellent model system as the ytterbium atom has only four strong 'fingerprint' transitions below 400 nm, together with one weak transition at 556 nm.

The absorption spectrum of ytterbium atoms isolated in argon matrices at 8 K has been studied in 200-800 nm region. The sharp absorptions in the 240-400 nm region can be well correlated with gas phase emission data. Matrix annealing and concentration studies allowed us to identify and characterize absorptions of the ytterbium dimer and higher associates in the 400-600 nm region. Prolonged irradiation into the ytterbium dimer and cluster absorptions demonstrated photostability of these products.

Irradiation into atomic absorptions of matrix isolated ytterbium atoms results in the appearance in the UV-vis spectrum of a second set of bands between 210 and 370 nm. These bands are very sharp - with halfwidths of 0.2 nm or less they strain the maximum resolution capability of our UV-spectrometer. These secondary bands cannot be attributed to associates, because they appear rapidly even in very diluted matrices.

Emission and excitation spectra of the isolated ytterbium atoms and the annealing / irradiation products were obtained parallel to the absorption spectra from the same samples. The excitation spectra clearly corroborate the presence of the new entity after irradiation into absorptions of isolated atoms. From an analysis of the ytterbium term scheme we propose the new entity to be an ytterbium ion, generated by means of two-photon absorption.

OBSERVATION OF SEVERAL NEW ELECTRONIC TRANSITIONS OF THE SrOH FREE RADICAL

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We report four new electronic transitions of the SrOH free radical, the $\tilde{C}^2\Pi - \tilde{X}^2\Sigma^+$, $\tilde{D}^2\Sigma^+ - \tilde{X}^2\Sigma^+$, $\tilde{E}^2\Sigma^+ - \tilde{X}^2\Sigma^+$ and $\tilde{F}^2\Pi - \tilde{X}^2\Sigma^+$ transitions. SrOH was prepared in a supersonic jet by laser ablation and spectra were recorded using laser-induced fluorescence. The $\tilde{C}^2\Pi - \tilde{X}^2\Sigma^+$ excitation spectrum shows complex vibronic structure which is attributed, at least in part, to Renner-Teller activity in the excited electronic state. This is supported by dispersed fluorescence spectra which show substantial bending mode activity in the emission from several different excited vibronic levels. It is suggested that the prominence of nominally forbidden vibrational features arises from a large change in permanent electric dipole moment between the \tilde{X} and \tilde{C} states. In turn, this suggests that the $\tilde{C}^2\Pi$ state of SrOH is the analogue of the reverse-polarised $^2\Pi$ states known for the alkaline-earth monohalides, i.e. the highest occupied π orbital points towards the O atom. The $\tilde{D}^2\Sigma^+ - \tilde{X}^2\Sigma^+$, $\tilde{E}^2\Sigma^+ - \tilde{X}^2\Sigma^+$ and $\tilde{F}^2\Pi - \tilde{X}^2\Sigma^+$ spectra are much simpler than the $\tilde{C} - \tilde{X}$ system, being dominated by activity in the Sr-O stretching vibration.

**DEVELOPMENT OF DOUBLE MODULATION
SUBMILLIMETER-WAVE SPECTROMETER: DETECTION OF
THE LOWEST PURE ROTATIONAL TRANSITION OF CH**

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A submillimeter-wave spectrometer system has been developed with backward wave oscillators as radiation sources. On top of usual frequency modulation, discharge or magnetic field modulation is superimposed to suppress the base line distortion which is a factor to limit the detection sensitivity of frequency modulation scheme in millimeter and submillimeter-wave regions. In this presentation, effectiveness of this method will be demonstrated by showing the spectra of several unstable species. Among them, the lowest pure rotational transition of CH was detected for the first time. Previously only the frequencies extrapolated to zero-field from Laser Magnetic Resonance spectra were available^a. For astrophysical purpose, our measurements provide much needed precise rest frequencies. These lines, however, are located right in the middle of a very strong atmospheric water absorption, and the astronomical detection will be facilitated by space submillimeter-wave observation.

^aJ. M. Brown and K. M. Evenson, *Astrophys. J.* **268**, L51-L56(1983)

A FULL DESCRIPTION OF THE POTENTIAL CURVE OF THE $B^1\Pi_u$ STATE OF ${}^7\text{Li}_2$, INCLUDING ITS POTENTIAL BARRIER

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Different experimental data have been combined to obtain a full description of the potential curve of the $B^1\Pi_u$ state of ${}^7\text{Li}_2$. From our experiment we observed with sub-Doppler resolution the excitation spectrum of the $B^1\Pi_u - X^1\Sigma_g^+$ system. We recorded transitions to $v' = 3-16$ in the $B^1\Pi_u$ state, including broad lines due to predissociation through the potential barrier. The molecular constants of Hessel and Vidal^a were used to generate transitions with $v' = 0-5$, to better describe the potential around the equilibrium internuclear distance. $F^1\Sigma_g^+ \rightarrow B^1\Pi_u$ transitions recorded in a dispersed fluorescence experiment^b gave supplementary information on many strongly predissociated levels up to $v' = 17$ of the $B^1\Pi_u$ state.

Accurate vibrational, rotational and distortion constants for the $B^1\Pi_u$ state were first obtained from a linear least-squares fit. Then the IPA method of Vidal and Scheingraber^c was used to generate a potential curve covering the bound and the quasibound region out to 5.6 Å of the $B^1\Pi_u$ state. An asymptotic calculation (based on parameters obtained from analysis of the long-range potential curve of the $A^1\Sigma_u^+$ state) gave the form of the outer part of the potential barrier (9-70 Å). The two pieces of the curve were linked by an analytical formula containing exchange and coulombic interactions.

Energies and linewidths can be predicted from this potential curve. Bound and quasibound energy levels up to $v' = 16$ are reproduced to within 0.005 cm^{-1} and those of the last vibrational level, $v' = 17$, (all of which are strongly predissociated), are reproduced to within 0.02 cm^{-1} . The linewidths of the quasibound levels have been reproduced to within 5%. The accurate sub-Doppler measurements of predissociated levels provide a rigorous test for the form of the outer part of the potential well.

^aM. M. Hessel, C. R. Vidal, *J. Chem. Phys.* 70, 4439 (1979)

^bI. Russier, F. Martin, C. Linton, P. Crozet, A. J. Ross, R. Bacis, and S. Churassy, *J. Mol. Spectrosc.* 168, 39 (1994)

^cC. R. Vidal, H. Scheingraber, *J. Mol. Spectrosc.* 65, 46 (1977)

THE HIGHLY EXCITED VIBRATIONAL DYNAMICS OF HCP, DCP AND HOCl

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Highly precise ab initio Potential Energy Surfaces have been computed recently for several triatomic molecules, including HCP/DCP [1] and HOCl [2]. The computed frequencies agree with the observed ones, whenever available, to within a few wavenumbers even for highly excited states with 30 (or more) quanta in the bending degree of freedom. The exact quantum wave functions for the first thousand states of each molecules have been examined visually, leading to the assignment of each level with three quantum numbers up to moderate energy values (typically 12000 cm^{-1} above the ground state). At this energies, wave functions with a completely new behavior appear. In the case of HCP, these new wave functions stretch along the Minimum Energy Path (MEP) leading to the unstable CPH isomer and in the case of HOCl along the MEP leading to the HO+Cl dissociation. It is shown here that in each of the three cases the appearance of the new states is due to a weak Fermi resonance, either between the bending and one stretching degrees of freedom (HCP and HOCl) or between the two stretching degrees of freedom (DCP). Moreover, the new states appear for those values of the remaining quantum numbers and the energy, for which the classical Hamiltonian displays a saddle-node bifurcation. The new wave functions stretch exactly along the stable Periodic Orbit born at the bifurcation.

[1] R. Schinke et al, to be published

[2] S. Skokov, K. A. Peterson and J.M. Bowman, J. Chem. Phys. 109, 2662 (1998)

MASS ANALYZED THRESHOLD IONIZATION SPECTROSCOPY OF P-FLUOROANILINE CATION

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Mass analyzed threshold ionization (MATI) and two-color resonant two-photon ionization (2C-R2PI) methods were used for detailed studies of the ionization threshold of p-fluoroaniline (PFA) and the vibrations of this molecule in the cationic ground state. The threshold ion spectra were recorded via the 0^0 vibrationless and the $6a^1$, 1^1 , 12^1 , $6a^11^1$, and $6a^112^1$ vibrational levels of the S_1 state. The adiabatic ionization energy of PFA is found to be $62\,543 \pm 4 \text{ cm}^{-1}$ by the MATI spectroscopy and $62\,550 \pm 7 \text{ cm}^{-1}$ by the 2C-R2PI spectroscopy. Results show that the active modes are mostly related to in-plane ring vibrations of the ion. All of these experimental data are presented for the first time. Ab initio and density functional theory calculations were also performed for predicting the ionization energy and vibrational frequencies. Comparative studies show that the measured and calculated results are in very good agreement.

THE MOLECULAR GEOMETRY AND QUADRUPOLE COUPLING CONSTANTS OF ClPO₂

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Gas phase ClPO₂ has been prepared using an electric discharge, and Fourier Transform microwave spectra of three of its isotopomers (³⁵ClPO₂, ³⁷ClPO₂ and ³⁵ClP¹⁸O¹⁶O) have been recorded. This work represents the first spectral observation of this unstable species in the gas-phase.

Although this molecule contains two non-zero spin nuclei, only the quadrupole coupling effects due to the chlorine nucleus have been analysed. The very small phosphorus nuclear spin-rotation splittings (on the order of ≈ 5 kHz) were purposefully suppressed because even in the highest resolution spectra recorded, these splittings were only partially resolved, thus making the spectra difficult to analyse and reliable transition frequencies difficult to obtain.

The determined centrifugal distortion corrected rotational constants have been used to derive r_0 and $r_{\Delta I/\Delta P}$ geometries; comparisons with (r_e) *ab initio* calculated values and with the experimentally determined ($r_0/r_s/r_e$) parameters of related species are given. The determined chlorine quadrupole coupling constants are compared to those of related molecules.

THE MICROWAVE SPECTRUM OF
1-CHLORO-2-METHYLPROPENE:
METHYL INTERNAL ROTATION AND $^{35,37}\text{Cl}$ NUCLEAR
QUADRUPOLE COUPLING

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Based on the data of Guirgis et al.^a the microwave spectrum of 1-chloro-2-methylpropene was reinvestigated.

Using pulsed molecular beam Fourier transform microwave (MB-FTMW) spectrometers in the range from 4-26 and 26-40 GHz it was possible to determine the rotational and centrifugal distortion constants, the hindering barriers to internal rotation of the two methyl tops, and the complete $^{35,37}\text{Cl}$ nuclear quadrupole coupling tensor.

Due to the good results for predicting hindering barriers of molecules with one internal rotor like 2-methyl-tolunitrile^b, 3-methyltolunitrile^c, and 4-methyltolunitrile^d by *ab initio* methods a potential surface depending on the two angles of internal rotation (α_1, α_2) was calculated.

By fitting the internal rotation potential function

$$V(\alpha_1, \alpha_2) = \frac{V_3}{2}(1 - \cos(3\alpha_1)) + \frac{V_3}{2}(1 - \cos(3\alpha_2)) + V_{12}\cos(3\alpha_1)\cos(3\alpha_2) + V'_{12}\sin(3\alpha_1)\sin(3\alpha_2) + \dots$$

to the calculated potential surface it was possible to compare the theoretical and experimental hindering barriers.

In addition to the information on internal rotation from the experimental data it was possible to get information about the top-top interaction termes (V_{12}, V'_{12}, \dots) from the calculated potential surface.

^aG. A. Guirgis, Y. S. Li, J. R. Durig, *J. Chem. Phys.* **75**, 3274-3287 (1981).

^bN. Hansen, H. Mäder, and T. Bruhn, *Mol. Phys.*, in press (1999).

^cT. Bruhn and H. Mäder, to be published.

^dU. Andresen, T. Bruhn, M. Gnida, H. Mäder, to be published.

WAVE PACKET DYNAMICS IN THE GROUND STATES OF DIATOMIC MOLECULES

NIKOLAI E. KUZ'MENKO, VADIM V. ERYOMIN and IGOR M. UMANSKII, *Department of Chemistry, Moscow State University, Leninskie Gory, Moscow 119899, Russia*

We present a new exactly solvable model, designed to analyze the dynamics of wave packets prepared in the ground state of a diatomic molecule by a sequence of two ultrashort light pulses. The model is based on radiation transitions between two displaced harmonic oscillators with different frequencies. The molecule is initially in the

lowest vibrational state of the ground electronic state. The first light pulse prepares the wave packet in the excited electronic state, whereas the second pulse which acts with some delay after the first pulse, transfers the molecule back to the ground state and creates the wave packet in this state. The light pulses are assumed to be infinitely short (δ -shaped).

This model contains the three parameters: (i) displacement between the oscillators, R , (ii) the ratio of frequencies, ω , and (iii) the time delay between the pulses, τ . The two former parameters are fixed in the experiment (they are molecular constants), whereas the latter parameter depends upon the experimental conditions and can be considered as the control parameter: variation of time delay enables one to control the properties of the wave packet in the ground state.

We obtained the exact expressions for the wave packets in the ground and excited state. We showed that both packets have the Gaussian form with the width and the center depending on R , ω , and τ . In particular, we showed that one can obtain the squeezed packets by selecting the proper time delay between the pulses: the minimum possible

width of the packet is ω^2 (ω is less than unity for most of diatomic molecules). We also determined the amplitudes of vibrations

and the number of states for both wave packets. These parameters are linear functions of displacement between the oscillators, R , and periodic functions of time delay τ for the packet in the ground state. We found that at specific time delays the amplitude of vibrations

and the energetic width of the ground state packet can be twice as large as those of the packet in the excited state. This result can be essential for optimal control of wave packet dynamics.

This work was supported by Russian Foundation for Basic Research (Grant no. 99-03-33283).

Invited Lectures P

Friday, September 10, 14:00

Chairman : A. TROMBETTI

SPECTRA OF VERY WEAKLY BOUND MOLECULAR COMPLEXES

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High resolution spectra of weakly bound complexes provide direct and remarkably precise measurements of intermolecular forces. The accurate calculation of these forces constitutes one of the frontiers of quantum chemistry, and the challenge from experiment helps to advance the theoretical state of the art. Conversely, reliable calculations help to interpret the spectra, which are sometimes difficult to assign because of the large amplitude internal motions involved.

At NRC, we produce weakly bound complexes using both supersonic jet expansion sources and equilibrium gas cells with long absorption paths at low temperatures. These are probed with tunable IR lasers or Fourier transform IR spectrometers. The (sometimes complementary) advantages and drawbacks of these techniques will be described.

Current studies of the CO dimer exemplify the challenges involved in high resolution IR spectroscopy of highly fluxional systems. The nature of this fundamental dimer remains an unsolved problem in spectroscopy. It was first detected twenty years ago in the microwave region by Klemperer's group.^a More recently the infrared spectrum, which appears in the 2140 cm^{-1} C-O stretch region, was observed in Bonn.^b Theory indicates that the CO-CO intermolecular potential has a number of minima differing in energy by small amounts and separated by small barriers, suggesting that it may not be helpful to think of a unique geometrical structure for the dimer.

We have extended the study of the IR spectrum using a rapid scan diode laser spectrometer with both planar and axisymmetric pulsed jet expansions. By probing the supersonic jet at varying distances downstream, we observed the (CO)₂ spectra over a range of effective rotational temperatures from about 12 down to 1 K, and were able to identify^c one perpendicular and two parallel bands with common lower state combination differences. Since obtaining those results, we have greatly extended the analysis, assigning over 120 lines to 13 subbands involving involving 24 lower state ($v_{CO} = 0$) and 36 upper state (v_{CO}

^aP.A. Vanden Bout, J.M. Steed, L.S. Bernstein, and W. Klemperer, *Astrophys. J.* **234**, 503 (1979).

^bM. Havenith, M. Petri, C. Lubina, G. Hilpert, and W. Urban, *J. Mol. Spectrosc.* **167**, 248 (1994).

^cM.D. Brookes and A.R.W. McKellar, *Chem. Phys. Lett.* **287**, 365 (1998).

= 1) rotational energy levels of the complex with total angular momentum values of $J = 0$ to 9.

The energy levels fall into two groups corresponding to distinct (but overlapping) 'isomers' with intermolecular separations of either about 4.0 or 4.4 Å. The 4.4 Å isomer is the ground state of the complex, while the 4.0 Å isomer is a very low-lying (0.88 cm^{-1}) excited state, but this energy ordering is inverted when $\nu_{CO} = 1$. Comparison with previous calculations suggests that both forms are planar and roughly T-shaped, with the 4.4 Å isomer in a C-bonded configuration and the 4.0 Å isomer in an O-bonded configuration.

In order to clarify the mystery of the CO dimer, we have turned to isotopic substitution. Measurements on a mixed dimer, $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$, indicate that the C-O vibrational coupling between monomer units is very weak. And study of the spectrum of $(^{13}\text{C}^{16}\text{O})_2$ shows that the energy of the 4.0 Å isomer relative to the 4.4 Å ground state *increases* by about 50% upon ^{13}C substitution.

**FREE JET ABSORPTION MILLIMETER WAVE
SPECTROSCOPY OF COMPLEX ROTATIONAL SPECTRA,
OF VAN DER WAALS AND OF HYDROGEN BONDED
ADDUCTS**

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Free jet absorption millimeter wave spectroscopy has only recently been extensively applied to obtain information on molecular systems. Here we report on:

1) The main differences with respect to the molecular beam Fourier transform microwave spectroscopy.

2) The results obtained on isolated molecules, like as: (i) the first assignment of the rotational spectrum of a molecule with two Iodine nuclei (heavy quadrupole coupling); (ii) molecules of biological interest; (iii) seven membered ring saturated molecules; (iv) molecules with several internal heavy rotors; (v) molecules with double minimum potential (severe Coriolis interactions); (vi) Complicated conformational equilibria.

3) On the information obtained on the structure, dynamics and energetics of Van der Waals and hydrogen bonded adducts. More in details we outline our recent results of a free jet millimeter wave absorption spectroscopy investigation of the dimers of difluoromethane, difluoroethane and difluoroethylene, and of their complexes with water, argon and neon. The Van der Waals motions generate an enormous distortion from the rigid rotor and occasionally doublings of the rotational lines, used to obtain the above mentioned information.

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ARNHEM 2001

10–14 September 2001

The Netherlands

<http://www.sci.kun.nl/mlf/HRMS17/>

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HRMS 17

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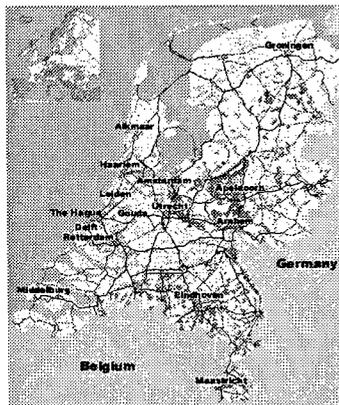
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The first circular of the

17th Colloquium on High Resolution Molecular Spectroscopy

to be held at the sport conference center Papendal at Arnhem

The Netherlands, September 10-14, 2001

will be spread by email, so please do not wait for a paper version!

If you plan to participate in the conference, or if you have not yet decided and would like to get the second circular, please (you must!) preregister by means of the fill-out-form on the www page mentioned above.

Finally, please pass on this information to other interested colleagues?

**55th OSU International Symposium
on Molecular Spectroscopy
June 12-16, 2000
Columbus Ohio, USA**

<http://molspect.mps.ohio-state.edu/symposium/>

Paper and email announcements concerning details of the 55th Symposium will be distributed early in 2000. Information will be continuously updated on the Symposium WWW site. As usual, the abstract deadline is March 1 and the Symposium server will open for their electronic receipt by late January, 2000.

25th EUROPEAN CONGRESS ON MOLECULAR SPECTROSCOPY

August 27th - September 1st, 2000
COIMBRA - PORTUGAL

http://qui.uc.pt/~rfausto/eucmos_xxv

The main purpose of EUCMOS XXV is to survey, at an advanced teaching level, recent progress in all major branches of molecular spectroscopy, involving methods and applications from theory to problem solving. All spectroscopic methods or techniques that provide information about the structure, dynamics, processes and properties of molecules or their aggregates, will be discussed.

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The Opening Lecture will be given by the 1996 Nobel Prize of Chemistry winner Prof. Sir Harold Kroto.



PRAHA2000

**The 16th International Conference on High
Resolution Molecular Spectroscopy
Prague, Czech Republic, September 3-7, 2000**

The subjects covered at this meeting are largely identical to those covered at the Sixteenth Colloquium on High Resolution Molecular Spectroscopy. The first circular will be distributed by electronic mail in September 1999. Printed copies of the circular will be available by request only.

Information is available from the executive chairman:

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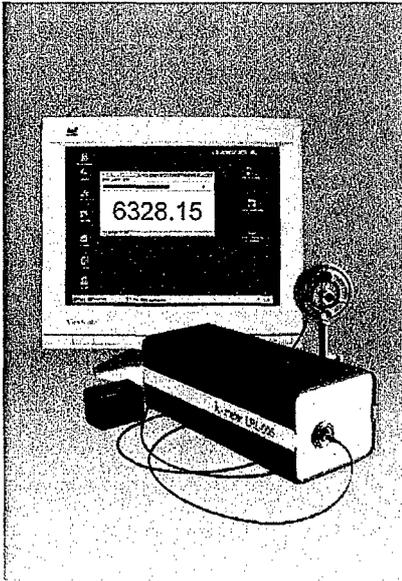
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The Sixteenth Colloquium on High Resolution Molecular Spectroscopy

DIJON 1999

DATES	06/09/1999	07/09/1999	08/09/1999	09/09/1999	10/09/1999
Hours	Monday	Tuesday	Wednesday	Thursday	Friday
9:00	Inv. speakers A	Inv. speakers E	Inv. speakers I	Inv. speakers K	Inv. speakers N
	+	+	+	+	+
11:00 - - 12:30	Poster Session B	Poster Session F	Poster Session J	Poster Session L	Poster Session O
	Lunch	Lunch	Lunch	Lunch	Lunch
14:00	Inv. speakers C	Inv. speakers G	Sight seeing tour	Free afternoon	Inv. speakers P
	+	+			
16:00 - - 17:30	Poster session D	Poster session H			
	Dinner	Town Hall reception		Dinner	
Evening			Banquet	Poster session M	



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