The Twenty-fourth Colloquium on High Resolution Molecular Spectroscopy

August 24 – 28, 2015

Université Bourgogne Franche-Comté

Dijon – FRANCE
The Twenty-fourth Colloquium on High Resolution Molecular Spectroscopy

HRMS DIJON 2015

August 24 – 28, 2015

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Administration-Management: Claire PRIOU-JACOTOT
(Claire.Priou@u-bourgogne.fr)

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O. FAUCHER P. HONVAULT J.-M. MULLER
T. GABARD B. LAVOREL S. PERNOT

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A. CSÁSZÁR M. HERMAN F. MERKT T. SOFTLEY
P. DE NATALE T. HUET J. ORPHAL J. TENNYSON
The HRMS DIJON 2015 Colloquium is supported by the institutions and companies listed below. They have made its organization possible.

Université de Bourgogne
Conseil Régional de Bourgogne
Ville de Dijon
Centre National de La Recherche Scientifique (CNRS)

BRUKER Optics
RADIANT DYES LASER
TAYLOR & FRANCIS / MOLECULAR PHYSICS
ELSEVIER
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We also wish to thank Pr. Terry A. MILLER (Ohio State University) who provided us with the EMSS software created by T. A. Miller and S. Panov for the OSU International Symposium on Molecular Spectroscopy. We used a modified version of this Electronic Abstract Submission program for the HRMS DIJON 2015 Colloquium.
# Program of the Colloquium

## Dates
- Aug. 24, 2015
- Aug. 25, 2015
- Aug. 26, 2015
- Aug. 27, 2015
- Aug. 28, 2015

## Hours

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<tr>
<th>Hours</th>
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<td>8:30</td>
<td>8:30 Welcome</td>
<td>Inv. Speakers E</td>
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<td>Chair: M. Herman</td>
<td>Molecular Physics</td>
<td>Planetary Atmospheres</td>
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<td>M. Quack*</td>
<td>Chair: A. Perin</td>
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<td>Inv. speakers C</td>
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<td>14:00 Sightseeing tour</td>
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<td>E. Cochener</td>
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<td>Chair: T. Huet</td>
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<td>Evening</td>
<td>Downtown conference</td>
<td>Breakfast</td>
<td>23:00 Bus to Dijon</td>
<td>Poster session O</td>
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**Note:** The Downtown Conference and the “Bar des Sciences” are planned additional events that will take place downtown for the Dijon people.

*Molecular Physics Lecture*
As in previous years there will be a special issue of the journal Molecular Physics published to mark the HRMS 2015 conference. All participants of the conference are invited to contribute a paper. This is not intended to be a conference proceedings, but rather a collection of original research papers, related to the conference themes and to material presented at the conference either as talks or posters. The papers will be refereed to the same standards as for normal papers submitted to the journal, and the volume will be edited by Tim Softley. The closing date for submissions will be Jan 31, 2016, but papers may be submitted at any time from the date of the conference onwards.

All papers will be published online with a DOI number as soon as they are ready for publication, and will not need to wait for the hard copy volume in which they will be brought together (to be published mid 2016).

All manuscripts will need to be submitted online via

http://mc.manuscriptcentral.com/tmph

To ensure submission to this special issue, please select ”Special issue paper” as manuscript type, select “HRMS2015” and choose “Tim Softley” as the editor.
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Program of Sessions
Invited Lectures A, Monday, August 24, 9:00

Chair: M. HERMAN

A1 – MOLECULES IN MOTION: SYMMETRIES AND INTRAMOLECULAR PRIMARY PROCESSES BETWEEN YOCOTSECONDS AND DAYS AS DERIVED FROM HIGH RESOLUTION SPECTROSCOPY AND THEORY (45 min.)
MARTIN QUACK
Molecular Physics Lecture.

A2 – ACCURACY IN SPECTROSCOPY (45 min.)
J. DEMAISON

Poster Session B, Monday, August 24, 11:00

B1 – HIGH-COHERENCE MID-INFRARED FREQUENCY COMB GENERATION AND APPLICATIONS
IACOPO GALLI, FRANCESCO CAPPELLI, PABLO CANCIO, GIOVANNI GIUSFREDI, DAVIDE MAZZOTTI, SAVERIO BARTALINI, PAOLO DE NATALE
Amat Mills Award Applicant.

B2 – SUB-MILLIMETER SPECTRUM AND ASTROPHYSICAL RESEARCH OF S-METHYL THIOFORMATE
A. JABRI, R. A. MOTIYENKO, J.-C. GUILLEMIN, L. MARGULÈS, I. KLEINER, B. TERCERO and J. CERNICHARO
Amat Mills Award Applicant.

B3 – CO$_2$ PRESSURE BROADENING AND SHIFT COEFFICIENTS FOR THE 2–0 BAND OF $^{12}$C$^{16}$O
R. HASHEMI, A. PREDOI-CROSS, A. C. VANDAELE, J. VANDER AUWERA
Amat Mills Award Applicant.

B4 – THE INTERNAL ROTATION OF FOUR METHYL GROUPS IN TETRAMETHYLTHIOPHENE
V. VAN, W. STAHL, A. R. PHILIPPS, H.V.L. NGUYEN
Amat Mills Award Applicant.

B5 – MOTION MANIPULATION OF AMMONIA AND 4-AMINOBENZONITRILE WITH MICROWAVE FIELDS
J. B. GRANEK, S. MERZ, T. BETZ and M. SCHNELL
Amat Mills Award Applicant.

B6 – THE ACETYL METHYL TORSION AND $^{14}$N QUADRUPOLE COUPLING IN N-ETHYLACETAMIDE AND N-ETHYLACETAMIDE-WATER COMPLEXES
R. KANNENGIESSER, M. J. LACH, W. STAHL, H. V. L. NGUYEN
Amat Mills Award Applicant.

B7 – SYMMETRY OF EXTREMELY FLOPPY MOLECULES: MOLECULAR STATES BEYOND ROTATION-VIBRATION SEPARATION
H. SCHMIEDT, S. SCHLEMMER, P. JENSEN
Amat Mills Award Applicant.
B8 – NEW OBSERVATIONS AND ANALYSIS OF THE EMISSION SPECTRUM OF THE $A^1\Pi \rightarrow X^1\Sigma^+$ BAND SYSTEM OF $^{12}$C$^{16}$O
M. OŚTROWSKA-KOPEC, I. PIOTROWSKA, M. ZACHWIEJA, R. KĘPA, R. HAKALLA, P. KOLEK, W. SZAJNA

B9 – SELF- AND CO$_2$-BROADENED LINE SHAPE PARAMETERS FOR THE $\nu_2$ AND $\nu_3$ BANDS OF HDO
V. M. DEVI, D. C. BENNER, K. SUNG, A. W. MANTZ, M. A. H. SMITH, R. R. GAMACHE, G. L. VILLANUEVA

B10 – LINE SHAPE PARAMETERS FOR NEAR INFRARED CO$_2$ BANDS IN THE 1.61 AND 2.06 $\mu$m SPECTRAL REGIONS
V. M. DEVI, D. C. BENNER, K. SUNG, L. R. BROWN, C. E. MILLER, T. J. CRAWFORD, A. W. MANTZ, M. A. H. SMITH

B11 – ANALYSIS OF RO-VIBRATIONAL SPECTRA USING A NEW AUTOMATED SPECTRAL ASSIGNMENT PROCEDURE (ASAP)
C. P. ENDRES, M. A. MARTIN-DRUMEL, M. C. McCARTHY, S. SCHLEMMER and S. THORWIRTH

B12 – THE SOLEIL VIEW ON SULFUR RICH OXIDES: THE $S_2$O BENDING ($\nu_2$) AND S–S STRETCHING ($\nu_3$) MODES AND THEIR ANALYSIS USING ASAP

B13 – TAMING THE ENFANT TERRIBLE: EXPERIMENTAL GROUND STATE COMBINATION DIFFERENCES OF CH$_4^+$
O. ASVANY, A. POTAPOV, S. BRÜNKEN, S. SCHLEMMER, K.M.T. YAMADA

B14 – AN ANALYTICAL MODEL OF THE DETECTION BANDWIDTH INFLUENCE ON ABSORPTION FREQUENCY AND LINELWIDTH MEASUREMENTS
F. ROHART, B. DARQUE and C. DAUSSY, A. CASTRILLO and L. GIANFRANI

B15 – CONFORMATIONAL MAP OF THE ANESTHETIC ENFLURANE

B16 – LINE LIST OF $^{15}$NH$_3$ IN THE RANGE 6369 TO 6578 CM$^{-1}$ AT ROOM TEMPERATURE
P. CACCANI, J. COSLEOU, M. KHELKHAL, J. EL ROMH, F. TAHER, P. CERMAK

B17 – EMPIRICAL POTENTIAL ENERGY SURFACES FOR THE ELECTRONIC GROUND STATES OF BrOH, C$_3$, AND HCO

B18 – DETECTION OF HSNO, A CRUCIAL INTERMEDIATE LINKING NO AND H$_2$S CHEMISTRIES

B19 – ENERGIES AND ELECTRIC PROPERTIES OF THE GROUND AND LOW-LYING EXCITED RbCs STATES
A. A. MEDVEDEV, A. V. ZAITSEVSKI and A. V. STOLYAROV

B20 – EQUILIBRIUM STRUCTURE OF PICOLINIC ACID FROM GAS ELECTRON DIFFRACTION DATA AND COUPLED CLUSTER CALCULATIONS
N. VOGT, I. I. MAROCHKIN, A. N. RYKOV
B21 – LOW-TEMPERATURE COLLISIONAL BROADENING IN THE FAR-IR CENTRIFUGAL DISTORTION SPECTRUM OF CH₄
V. BOUDON, J. VANDER AUWERA, L. MANCERON, F. KWABIA TCHANA, T. GABARD, B. AMYAY, M. FAYE

B22 – ROTATIONAL STUDY OF THE CH₄–CO VAN DER WAALS COMPLEX IN THE MILLIMETER-WAVE RANGE
I. V. TARABUKIN, V. A. PANFILOV, L. SURIN, S. SCHLEMMER

B23 – LARGE AMPLITUDE MOTION IN DIPHENYL ETHER
C. MEDCRAFT, S. ZINN, M. SCHNELL

B24 – RYDBERG STATES OF ATOMIC OXYGEN FROM INFRARED FTIR SPECTROSCOPY
SVATOPLUK CIVIS, MARTIN FERUS, PETR KUBELOK, ADAM PASTOREK, EKATERINA M. ZANOZINA, LIBOR JUHA, VLADISLAV E. CHERNOV, ANASTASIA A. VO-RONINA

B25 – FIRST ORDER STARK EFFECT AND TORSIONAL MOTION INTERACTION IN H₂O₂
L. H. COUDERT and C. GUTLÉ

B26 – HIGH-RESOLUTION STUDY OF THE ROVIBRATIONAL SPECTRUM OF PF₃ IN THE 350 AND 690 cm⁻¹ REGIONS: NEW SOLUTIONS FOR OLD TOPICS
ADINA CEAUSU-VELCESCU, PETR PRACNA, JÜRGEN BREIDUNG and WALTER THIEL, MOHAMED BADAOUI

B27 – INFRARED CROSS-SECTIONS OF NITRO-DERIVATIVE VAPORS: NEW SPECTROSCOPIC SIGNATURES OF EXPLOSIVE TAGGANTS AND DEGRADATION PRODUCTS
A. CUISSET, G. MOURET, O. PIRALI, S. GRUET, G. P. PIAU, G. FOURNIER

B28 – AB INITIO CALCULATION OF ENERGY LEVELS AND RO-VIBRATIONAL SPECTRA FOR GeH₄ MOLECULE
A. V. NIKITIN, A.A. RODINA, M. REY, VI.G. TYUTEREV

B29 – THE VIBRATIONAL SPECTRA OF 1-CHLORO-1,1-DIFLUOROETHANE (HCFC-142b) INVESTIGATED BY A COMBINED EXPERIMENTAL AND COMPUTATIONAL APPROACH
A. PIETROPOLLI CHARMET, M. PAULETTI, P. STOPPA, N. TASINATO, S. GIORGIANNI, C. PUZZARINI, J. BLOINO, M. BICZYSKO

B30 – HIGH RESOLUTION INFRARED SPECTRUM AND EQUILIBRIUM STRUCTURE OF BF₂OH
J. DEMAISON, H.D. RUDOLPH, A. PERRIN, N. VOGT, H. BÜRGER

B31 – PRECISE ABSORPTION AND DISPERSION MEASUREMENTS IN HIGH-FINESSE OPTICAL CAVITIES
A. CYGAN, P. WCIŚLO, S. WÓJTEWICZ, M. ZABOROWSKI, P. MASŁOWSKI, R. CIURYSŁO, D. LISAK, J. T. HODGES, R. GUO

B32 – MULTI-SPECTRUM ANALYSIS OF METHANE IN THE ν₁+ν₄ AND ν₃+ν₄ BANDS: TEMPERATURE DEPENDENCES OF SELF- AND AIR-BROADENED LINE PARAMETERS

B33 – DYNAMICAL MOLECULAR STRUCTURE OF THE CO₂-DMS COMPLEX INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY
YOSHIYUKI KAWASHIMA, SAKAE IWANO, EIZI HIROTA
Invited Lectures C, Monday, August 24, 14:00,
Mini-Symposium, New experiments with cold molecules

Chair : Th. HUET

C1 – APPLICATIONS OF COLD MOLECULES TO FUNDAMENTAL PHYSICS (30 min.)
M. R. TARBUtT

C2 – MOLECULE CHIP: TOWARD HIGH RESOLUTION SPECTROSCOPY (30 min.)
S. BORRI, G. INSERO, P. DE NATALE, G. SANTAMBROGIO

C3 – OPTICAL PARAMETRIC OSCILLATOR FOR AVANT-GARDE HIGH RESOLUTION SPECTROSCOPY (30 min.)
I. RICCIARDI

Poster Session D, Monday, August 24, 16:00

D1 – A ROOM TEMPERATURE LINELIST FOR HYDROGEN PEROXIDE
A. F. AL-REFAI, S. N. YURCHENKO, O. L. POLYANSKY, J. TENNYSON
Amat Mills Award Applicant.

D2 – CAVITY ENHANCED MID-IR/NEAR-IR DOUBLE RESONANCE DETECTION OF ACETYLENE SYMMETRIC STATES
J. KARHU, J. NAUTA, M. VAINIO, M. METSÄLÄ, L. HALONEN
Amat Mills Award Applicant.

D3 – HIGH ACCURACY CO$_2$ LINE INTENSITIES
Amat Mills Award Applicant.

D4 – UNRAVELLING THE CONFORMATIONAL LANDSCAPE OF NICOTINOIDS: THE STRUCTURE OF COTININE IN THE GAS PHASE
I. URIARTE, P. ÉCIJA, E. J. COCINERO, C. PÉREZ, E. CABALLERO-MANCEBO, A. LESARRI
Amat Mills Award Applicant.

D5 – DIRECT COMPARISON OF PDH AND SWEPT LOCKING SCHEMES FOR CAVITY-ENHANCED ABSORPTION SPECTROSCOPY
G. KOWZAN, M. PARADOWSKA, M. BORKOWSKI, P. ABLEWSKI, SZ. WÓJTÉWICZ, K. STEC, D. LISAK, R. S. TRAWIŃSKI, P. MASŁOWSKI, K. F. LEE, M. E. FERMANN
Amat Mills Award Applicant.

D6 – NEW HIGH TEMPERATURE LINELIST FOR CHROMIUM HYDRIDE
M. N. GORMAN, S. N. YURCHENKO, L. LODI, J. TENNYSON
Amat Mills Award Applicant.

D7 – STUDY OF Cs D$_2$ LINE ATOMIC TRANSITIONS IN STRONG TRANSVERSE MAGNETIC FIELDS BY AN OPTICAL HALF-WAVELENGTH CELL
C. LEROY, Y. PASHAYAN-LEROY, A. SARGSYAN, A. AMIRYAN, G. HAKHUMYAN, D. SARKISYAN
D8 – ON DECOUPLING OF TOTAL ELECTRONIC ANGULAR MOMENTUM AND NUCLEAR SPIN FOR $^{39}$K ATOM
C. LEROY, Y. PASHAYAN-LEROY, A. SARGSYAN, A. TONOYAN, G. HAKHUMYAN, D. SARKISYAN

D9 – SELECTIVE REFLECTION FROM DENSE Rb$_2$ MOLECULAR VAPOR
A. PAPOYAN, A. SHMAVONYAN, A. KHANBEKYAN, M. MOVSISYAN

D10 – ON-LINE MEASUREMENT OF GASEOUS IODINE DURING A PWR SEVERE ACCIDENT
I. HAYKAL and D. DOIZI, A. PERRIN and F. KWABIA TCHANA, V. BOUDON, L. MANCERON, G. MEJEAN, G. DUCROS

D11 – ON THE "EXPANDED LOCAL MODE" APPROACH APPLIED TO ETHYLENE
O. N. ULENIKOV, E. S. BEKHTEREVA, A. L. FOMCHENKO, A. S. BÉLOVA, Yu. V. KRIVCHIKOVA

D12 – HIGH RESOLUTION ANALYSIS OF THE $v_4$, $v_7$ and $v_{12}$ VIBRATIONAL BANDS OF C$_2$D$_4$
O. N. ULENIKOV, O. V. GROMOVA, E. S. BEKHTEREVA, A. L. FOMCHENKO, F. ZHANG, S. BAUERECKER, C. MAUL

D13 – HIGH RESOLUTION SPECTROSCOPIC STUDY OF THE C$_2$H$_2$D$_2$- cis SPECTRA IN THE REGION OF 580-1210 cm$^{-1}$: $v_4$, $v_6$, $v_7$, $v_8$ and $v_{10}$ VIBRATIONAL BANDS
O. N. ULENIKOV, E. S. BEKHTEREVA, O. V. GROMOVA, Yu. V. CHERTAVSKIKH, I. A. KONOV, C. MAUL, S. BAUERECKER,

D14 – FIRST INVESTIGATION OF THE HERZBERG (C$^3\Sigma^+ \rightarrow A^1\Pi$) SYSTEM IN THE $^{12}$C$^{17}$O AND A GLOBAL ISOTOPIC ANALYSIS OF THE C$^3\Sigma^+$ RYDBERG STATE
R. HAKALLA, W. SZAJNA, M. ZACHWIEJA, P. KOLEK, M. OSTROWSKA-KOPEĆ, I. PIOTROWSKA, and R. KĘPA

D15 – KINETIC AND SPECTROSCOPIC STUDIES OF OZONE USING DOPPLER LIMITED ABSORPTION SPECTROSCOPY AT 28 THz WITH A FREE RUNNING DFB QUANTUM CASCADE LASER
MARCO MINISSALE, THOMAS ZANON-WILLETTE, PASCAL JESECK, HADJ ELANDALOSSI, CHRISTIAN ROUILLÉ, PATRICK MARIE-JEANNE, YAO TÉ, CORINNE BOURSIER, CHRISTOF JANSSEN

D16 – SYNCHROTRON-BASED HIGH RESOLUTION STUDY OF THE LOW FREQUENCY VIBRATIONAL MODES OF THREE PANHS: QUINOXALINE, QUINAZOLINE AND INDOLE
S. GRUET, O. PIRALI, M. GOUBET

D17 – HIGH RESOLUTION SPECTROSCOPY OF SOCl$_2$ AND ITS ISOTOPOLOGUES: FROM THE MICROWAVE TO THE FAR-INFRARED

D18 – SEMICLASSICAL LINE BROADENING CALCULATIONS WITH POTENTIAL ENERGY SURFACE: APPLICATION TO COLLISIONAL EXCITATION OF NH$_3$ BY Ar
C. AYARI, J. LOREAU, M. DHIB, C. DAUSSY, F. THIBAULT, H. AROUI

D19 – TUNNELING IN MOLECULES PROBED BY HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY
K. DULITZ, U. HOLLENSTEIN, F. MERKT

D20 – SPIN-ORBIT COUPLING EFFECT IN LOW-LYING STATES OF KRb
V. V. MESHKOV, A. V. STOLYAROV and E. A. PAZYUK
D21 – ROTATIONAL SPECTROSCOPY OF 4-HYDROXY-2-BUTYNYLITRILE
R. A. MOTIYENKO, L. MARGULÉS, J.-C. GUILLAUME

D22 – AB-INITIO STUDY OF THE I, I' AND I'' 3Πu SUPEREXCITED STATES OF O₂
G. J. VÁZQUEZ, H. P. LIEBERMANN, H. LÉFEBVRE-BRION

D23 – MICROWAVE SPECTROSCOPIC AND QUANTUM CHEMICAL INVESTIGATIONS ON DIMETHYL 1,1-CYCLOPROPANEDICARBOXYLATE
J. SCHÜTT, V. VAN, W. STAHL, H. V. L. NGUYEN

D24 – NEW SPECTRA OF SO₂F₂ BELOW 1000 cm⁻¹
F. HMIDA, B. GROUIEZ, M. ROTGER, V. BOUDON, L. MANCERON, H. AROUI

D25 – QUANTUM MECHANICAL CALCULATION OF THE MOBILITY OF THE C ION IN A COOLED He GAS AT 4.3 K
L. AISSAOUI, M. BOULEDROUA and K. ALJOUA

D26 – MEASUREMENT AND MODELING OF COLD ¹³CH₄ SPECTRA FROM 2.1 TO 2.7 μM

D27 – PSEUDOROTATIONAL LANDSCAPE OF SEVEN-MEMBERED RINGS: THE CONFORMATIONAL FLEXIBILITY OF ε-CAPROLACTONE

D28 – METHANE HIGH-T PARTITION FUNCTION FROM CONTACT TRANSFORMATIONS AND VARIATIONAL CALCULATIONS
B.M. KRISHNA, A.V. NIKITIN, S.A. TASHKUN, M. REY, V.L.G. TYUTEREV

D29 – HIGH RESOLUTION OBSERVATIONS OF OH AND SH IN TRANSLUCENT INTERSTELLAR CLOUDS
D. ZHAO, H. LINNARTZ, G.A. GALAZUDINOV, J. KRELOWSKI

D30 – LINE BROADENING CALCULATIONS FOR METHANE PERTURBED BY DIATOMIC MOLECULES
T. GABARD

D31 – ANHARMONIC EFFECTS IN VIBRATIONAL LIGHT-SCATTERING PHENOMENA
Y. CORNATON, M. RINGHOLM, K. RUUD

D32 – A RAPID METHOD FOR CALCULATION OF RO-VIBRATIONAL SPECTRA OF LARGE MOLECULES
A. I. PAVLYUCHKO, S. N. YURCHENKO, J. TENNYSON

D33 – STUDY OF HIGH RESOLUTION RO-VIBRATIONAL SPECTRA OF THE CH₂=CD₂ MOLECULE: SET OF THE LOWEST FUNDAMENTAL BANDS
O. N. ULENIKOV, O. V. GROMOVA, E. S. BEKHTEREVA, K. B. BEREZKIN, N. V. KASHIRINA, S. BAUERECKER, C. SYDOW, T. L. TAN
Invited Lectures E, Tuesday, August 25, 9:00, Mini-Symposium, Spectroscopy of planetary atmospheres

Chair: A. PERRIN

E1 – SPECTROSCOPIC SIGNATURE OF ORGANIC MOLECULES IN TITAN’S ATMOSPHERE (30 min.)
A. JOLLY

E2 – ACCURATE REMOTE SENSING OF GREENHOUSE GASES IN THE EARTH’S ATMOSPHERE (30 min.)
ANDRÉ BUTZ

E3 – NATURAL AND ANTHROPOGENIC CONTRIBUTIONS TO THE ATMOSPHERIC COMPOSITION VARIABILITY AS OBSERVED FROM SPACE (30 min.)

Poster Session F, Tuesday, August 25, 11:00

F1 – METHANOL OH-STRETCH OVERTONE: TWO TEMPERATURE TECHNIQUE IN THE JET
V. SVOBODA, J. RAKOVSKÝ, V. HORKÁ-ZELENKOVÁ, P. PRACNA, and O. VOTAVA
Amat Mills Award Applicant.

F2 – FIRST HIGH-RESOLUTION OVERTONE DATA FOR TRANS-FORMIC ACID IN THE SUPersonic JET
V. SVOBODA, J. RAKOVSKÝ, V. HORKÁ-ZELENKOVÁ, P. PRACNA, and O. VOTAVA
Amat Mills Award Applicant.

F3 – SYNCHROTRON-BASED HIGH RESOLUTION STUDY OF PROTONATED SPECIES ON THE AILES BEAMLINE
S. GRUET and O. PIRALI
Amat Mills Award Applicant.

F4 – ACCURATE FIRST-PRINCIPLES SPECTRA PREDICTIONS FOR ETHYLENE FROM FULL 12D AB INITIO SURFACES
T. DELAHAYE, A. V. NIHITIN, M. REY, V. G. TYUTEREV, P. G. SZALAY
Amat Mills Award Applicant.

F5 – POLARIZATION ROTATION IMPACT-FT-MW SPECTROMETER
D. WACHSMUTH, J.-U. GRABOW
Amat Mills Award Applicant.

F6 – UNRAVELLING THE MOLECULAR MECHANISMS OF SMELL WITH BROADBAND ROTATIONAL SPECTROSCOPY
DONATELLA LORI, MIGUEL A. BERMÚDEZ and M. EUGENIA SANZ
Amat Mills Award Applicant.

F7 – SMALL MOLECULES IN EXTERNAL MAGNETIC FIELDS
H. MEDEL COBAXIN, A. ALLIJA, J. C. LOPEZ VIEYRA, A. TURBINER
F8 – VIBRATIONAL STATES OF THE TRIPLET ELECTRONIC STATE OF H$_3^+$: THE ROLE OF NON-ADIABATIC JAHN-TELLER COUPLING
A. ALIJAH, V. KOKOOUINE

F9 – ACCURATE NON-ADIABATIC CORRECTIONS TO RO-VIBRATIONAL LEVELS OF SMALL MOLECULES THROUGH EFFECTIVE NUCLEAR MASSES
J. R. MOHALLEM, L. G. DINIZ, L. Adamowicz, A. ALIJAH

F10 – FITS USING A NEW HYBRID PROGRAM OF THE MW SPECTRA OF 2-METHYL-MALONALDEHYDE AND AMMONIA-WATER COMPLEX
ISABELLE KLEINER, JON T. HOUGEN

F11 – STRONG THERMAL NONEQUILIBRIUM IN HYPERSONIC CO AND CH$_4$ PROBED BY CRDS
M. LOUVIOT, N. SUAS-DAVID, V. BOUDON, R. GEORGES, M. REY, S. KASSI

F12 – INFRARED SPECTROSCOPY OF RUTHENIUM TETROXIDE AND HIGH-RESOLUTION ANALYSIS OF THE $\nu_3$ BAND
S. REYMOND-LARUINAZ and D. DOIZI, L. MANCERON, V. BOUDON

F13 – DUO: A GENERAL MULTI-STATE PROGRAM FOR SOLVING THE NUCLEAR MOTION SCHRODINGER EQUATION FOR DIATOMIC MOLECULES WITH ARBITRARY COUPLINGS
S. N. YURCHENKO, L. LODI, J. TENNYSON, A. STOLYAROV

F14 – MODELLING HIGH-RESOLUTION ABSORPTION SPECTRA WITH EXOMOL LINE LISTS: NH$_3$ AND CH$_4$
E. J. BARTON, J. TENNYSON, S. N. YURCHENKO, A. FATEEV and S. CLAUSEN

F15 – TEMPERATURE DEPENDENCE OF CO$_2$-COLLISIONAL BROADENING OF ACETYLENE LINES
L. FISSIAUX, M. LEPÈRE

F16 – N$_2$-COLLISIONAL BROADENING OF METHANE LINES AT LOW AND HIGH TEMPERATURES
B. VISPOEL, M. LEPÈRE

F17 – PRESSURE BROADENING AND SHIFTING COEFFICIENTS AS TESTS OF H$_2$(D$_2$)-He POTENTIAL ENERGY SURFACES
F. THIBAULT, P. WCISLO, and R. CIURYLO

F18 – MILLIMETER-WAVE MEASUREMENTS AND AB INITIO CALCULATIONS OF THE NH$_3$–CO COMPLEX
L. A. SURIN, A. POTAPOV, S. SCHLEMMER, A. A. DOLGOV, I. V. TARABUKIN, V. A. PANFILOV, Y. N. KALUGINA, A. FAURE, A. VAN DER AVOIRD

F19 – RELEASE OF THE MOGADOC UPDATE WITH AN ENHANCED 3D-VIEWER
J. Vogt, E. POPOV, R. RUDERT, N. Vogt

F20 – EMISSION SPECTROSCOPY OF THE $A^1\Pi$ – $X^1\Sigma^+$ SYSTEM OF THE AID ISOTOPOLOGUE

F21 – PROBING COLLISIONAL RELAXATION DYNAMICS IN CO$_2$ GAS MIXTURES THROUGH FIELD-FREE MOLECULAR ALIGNMENT
F. CHAUSSARD, Th. VIEILLARD, F. BILLARD, O. FAUCHER, B. LAVOREL, D. SUGNY, J.-M. HARTMANN, C. BOULET
F22 – MIPAS DATABASE: NEW HNO₃ LINE PARAMETERS AT 7.6 MICRONS DERIVED FROM LABORATORY INTENSITY MEASUREMENTS AND MIPAS SATELLITE SPECTRA
A. PERRIN, J.-M. FLAUD, M. RIDOLFI, J. VANDER AUWERA, M. CARLOTTI

F23 – THE WATER SELF- AND FOREIGN- CONTINUUM IN THE 2.3 AND 1.6 MICRONS ATMOSPHERIC WINDOWS
D. MONDELAIN, S. VASILCHENKO, S. KASSI, D. ROMANINI, I. VENTRILLARD, A. CAMPARGUE

F24 – ROTATIONAL SPECTRUM OF THE NH₃–H₂ VAN DER WAALS COMPLEX
L. A. SURIN, I. V. TARABUKIN, S. SCHLEMMER, A. BREIER, T. GIESEN, M. C. MCCARTHY

F25 – VARIATIONAL CALCULATION OF SENSITIVITY COEFFICIENTS TO PROBE A VARIABLE PROTON-TO-ELECTRON MASS RATIO
A. OWENS, S.N. YURCHENKO, W. THIEL, V. ŠPIRKO

F26 – EXPERIMENTAL AND THEORETICAL STUDYING OF VAN DER WAALS CO₂ CLUSTERS FOR PLANETARY ATMOSPHERES MODELLING
T. N. SINYAKOVA, J. V. BULDYREVA, E. ASPIN, D. V. OPARIN, N.N. FILIPPOV

F27 – A NEW LINELIST FOR HOT VO: CHALLENGES AND PROGRESS
L. K. MCKEMMISH, S. N. YURCHENKO, J. TENNYSON

F28 – HIGH RESOLUTION ANALYSIS OF THE ν₁ AND ν₅ BANDS OF PHOSGENE ³⁵Cl₂CO AND ³⁵Cl²³⁷ClCO
F. KWABIA TCHANA, J. -M. FLAUD, M. NDAO, W. LAFFERTY, L. MANCERON

F29 – CLASSICAL TRAJECTORY STUDIES OF CH₄ METASTABLE DIMERS FORMED IN COLLISIONS WITH NOBLE ATOMS
SERGEY V. IVANOV

F30 – AB INITIO VARIATIONAL PREDICTIONS FOR HIGH-RESOLUTION LASER SPECTROSCOPY. ASSIGNMENT OF 107 NEW SUB-BANDS OF METHANE IN THE ICOSAD RANGE 6280-7800 CM⁻¹
M. REY, A. V. NIHITIN, A. CAMPARGUE, S. KASSI, D. MONDELAIN, VI.G. TYUTEREV

F31 – AN INTENSITY STUDY OF THE TORSIONAL BANDS OF ETHANE AT 35 MICRON

F32 – RELATIVISTIC DEFORMATION OF SPECTROSCOPIC LINE SHAPES
P. WCISLO, R. CIURYLO, P. AMODIO, L. GIANFRANI

F33 – ANALYSIS OF HIGH RESOLUTION RO-VIBRATIONAL SPECTRUM OF THE CH₂=CHD MOLECULE IN THE REGION OF 2800 – 3300 CM⁻¹: THE ν₁ + ν₂, ν₂ + ν₁₂, ν₁, ν₂, ν₇ + ν₁₁ AND ν₇ BANDS
O. N. ULENIKOV, E. S. BEKHTEREVA, O. V. GROMOVA, S. A. ZHDANOVICH, T. L. TAN, M. G. GABONA
Invited Lectures G, Tuesday, August 25, 14:00

Chair : J. U. GRABOW

G1 – CAVITY-ENHANCED FREQUENCY COMB SPECTROSCOPY (45 min.)
JUN YE

G2 – PHYSICS BEYOND THE STANDARD MODEL FROM MOLECULES (45 min.)
Wim UBACHS

Poster Session H, Tuesday, August 25, 16:00

H1 – ROUTINE CAVITY RING DOWN SPECTROSCOPY WITH SUB-MHZ ABSOLUTE FREQUENCY CALIBRATION

H2 – OPTICAL FEEDBACK FREQUENCY-STABILIZED CRDS FROM ACCURATE LINE PROFILES TO SATURATED ABSORPTION
S. KASSI, J. BURKART

H3 – HIGH SENSITIVITY CW-CAVITY RING DOWN SPECTROSCOPY OF N₂O NEAR 1.22 µm
E. V. KARLOVETS, A. CAMPARGUE, S. KASSI, S. A. TASHKUN, V. I. PEREVALOV

H4 – THE MILLIMETER-WAVE SPECTRA OF METHACROLEIN AND METHYL VINYL KETONE. TORSION-ROTATION-VIBRATION EFFECTS IN THE EXCITED STATES

H5 – HIGH RESOLUTION HETERODYNE DETECTION REVEALS THE DISCRETE NATURE OF COHERENT SYNCHROTRON EMISSION AS A HIGH DENSITY FREQUENCY COMB THZ SOURCE
S. TAMMARO, O. PIRALI, P. ROY, J.-F. LAMPIN, G. DUCOURNAU, A. CUISSET, F. HINDLE, G. MOURET

H6 – SPECTROSCOPY OF ¹⁴NH₃ IN THE 2.3 MICRON RANGE: ASSIGNMENTS OF HOT BANDS
P. CACCIANI, J. COSLEOU, M. KHELKHAL, P. CERMACK, J. HOVORKA, P. VEIS

H7 – HIGH RESOLUTION ANALYSIS OF S¹⁸O₂ AND S¹⁶O¹⁸O SPECTRUM: THE ν₁ AND ν₃ INTERACTING BANDS
O. N. ULENIKOV, E. S. BEKHTEREVA, V. A. ZAMOTAeva, Yu. V. KRIVCHIKova, S. BAUERECKER, T. BUTTERSACK, C. SYDOW

H8 – A HIGH RESOLUTION ANALYSIS OF 2ν₂/ν₂ +ν₄/2ν₄ BANDS OF GeH₄ (M=76,74)
O. N. ULENIKOV, O. V. GROMOVA, E. S. BEKHTEREVA, N. I. RASPOPOVA, M. A. KOSHELEV, A. P. VELMUZOVA, I. A. VELMUZOVA, P. G. SENNIKOV

H9 – DISPERSED FLUORESCENCE SPECTROSCOPY OF THE B ²E′ – X ²A′₂ TRANSITION OF ¹⁴NO₂ AND ¹⁵NO₂
MASARU FUKUSHIMA and TAKASHI ISHIWATA

H10 – ABSORPTION SPECTRUM OF WATER VAPOR IN THE 3-5 MICRONS TRANSPARENCY WINDOW
T.M. PETROVA, A.M. SOLODOV, A.A. SOLODOV and O.V. NAUMENKO
H11 – HIGH-RESOLUTION SPECTROSCOPY AND ANALYSIS OF VARIOUS BANDS OF CF₄ TO ELUCIDATE ITS HOT BAND STRUCTURE
M. CARLOS, V. BOUDON, M. LOÈTE, M. ROTGER, X. THOMAS, P. SOULARD, O. PIRALI, M. GOUBET, R. GEORGES, T. HUET, P. ASSELIN,

H12 – MODELING OF THE TRIAD \(v_8, v_1, v_6\) AND THE \(v_2\) BAND OF SULFURYL FLUORIDE USING THE \(C_2\varepsilon\) TOP DATA SYSTEM (\(C_2\varepsilon\) TDS) : FREQUENCY ANALYSIS
F. HMIDA, T. COURS, M. REY, M. ROTGER, V. BOUDON, H. AROUI

H13 – A COMBINED GIGAHERTZ AND TERAHERTZ SYNCHROTRON-BASED FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDY OF PHENOL AND META- AND ORTHO-D-PHENOL: PROBING TUNNELING SWITCHING DYNAMICS
ZIQIU CHEN, SIEGHARD ALBERT, R. PRENTNER and MARTIN QUACK

H14 – THEORETICAL REIMS-TOMSK SPECTROSCOPIC LINE LISTS (THEORETS) FOR MOLECULES OF PLANETOLOGICAL AND ASTROPHYSICAL INTEREST
M. REY, A. V. NIKITIN, Y. BABIKOV, E. STARIKOVA, S. TASHKUN, Y. S. CHIZHMAKOVA, A. A. RODINA, Y. A. IVANOVA, VI. G. TYUTEREV

H15 – A DEUTERATED WATER ISOTOPOLOGUE DATABASE TO AID LABORATORY MEASUREMENTS AND MARS ORBITER MISSIONS
R. GAMACHE, C. RENAUD, M. FARESE

H16 – HIGH RESOLUTION INFRARED SPECTROSCOPY OF ASTROPHYSICALLY RELEVANT MOLECULAR CATIONS
K.D. DONEY, D. ZHAO, H. LINNARTZ

H17 – SELF-AND \(N_2\)-BROADENING COEFFICIENTS OF CH₃I ROVIBRATIONAL LINES IN THE \(v_5\) BAND
A. BOUGHDIRI, M. ROTGER, H. AROUI

H18 – CONTINUOUS-WAVE LASER AND OPTICAL FREQUENCY COMB CAVITY-ENHANCED SPECTROSCOPY OF CO AT 1.58 \(\mu\)m

H19 – WATER VAPOR CONTINUUM IN THE RANGE OF ROTATIONAL SPECTRUM OF \(H_2O\) MOLECULE: NEW EXPERIMENTAL DATA AND THEIR COMPARATIVE ANALYSIS
M. TRETYAKOV, T. ODINTSOVA, P. ROY, O. PIRALI

H20 – ON THE CALCULATIONS OF THE INFLUENCE OF A COLLISIONAL CORRELATION ON THE DICKE NARROWING OF A SPECTRAL LINE SHAPE
H. CYBULSKI, R. CIURYLO

H21 – ASSIGNMENTS OF \(^{15}\)NH₃ TRANSITIONS IN THE 2.3 MICRON RANGE
J. HOVORKA, P. ČERMÁK, P. VEIS, P. CACCIANI, J. COSLÉOU

H22 – CALIBRATION-FREE MEASUREMENTS OF ROTATIONAL TEMPERATURE IN ATMOSPHERIC DISCHARGES BY THE \(N_2\) HERMAN INFRARED SYSTEM
P. ČERMÁK, A. ANNUSOVÁ, J. KRISTOF, J. HOVORKA, P. VEIS, J. RÁKOVSKÝ

H23 – GENERALIZED HYPER-RAMSEY RESONANCE WITH SEPARATED OSCILLATING FIELDS
THOMAS ZANON-WILLETTE, MARCO MINISSALE, VALERA YUDIN, ALEXEY TAI-CHENACHEV
H24 – TUNNELING EFFECTS IN ROTATIONAL SPECTRA OF CONFORMERS OF METHYL SALICYLATE - WATER
SUPRIYA GHOSH, JAVIX THOMAS, YUNJIE XU, WOLFGANG JÄGER

H25 – THE INTERPLAY OF INTRA- AND INTERMOLECULAR HYDROGEN BONDS IN PROLINOL AND ITS COMPLEXES WITH WATER
DONATELLA LORU, M. EUGENIA SANZ, CRISTÓBAL PÉREZ, LUCA EVANGELISTI, BROOKS H. PATE

H26 – GLYCOLALDEHYDE DIMER: MOLECULAR RECOGNITION OF SIMPLE SUGARS IN THE GAS-PHASE
S. ZINN, C. MEDCRAFT, T. BETZ, M. SCHNELL

H27 – HIGH ACCURACY COMPUTED LINE LISTS FOR H217O AND H218O
O. L. POLYANSKY, L. LODI, J. TENNYSON, A. A. KYUBERIS, R. I. OVSYANNIKOV and N. F. ZOBOV

H28 – CALCULATION OF A COMPLETE WATER LINELIST UP TO DISSOCIATION
O. L. POLYANSKY, J. TENNYSON, L. LODI, A. A. KYUBERIS, N. F. ZOBOV

H29 – ELECTRONIC ENERGY TRANSFER IN NaK : IDENTIFICATION OF A1Σ+ –X1Σ+ TRANSITIONS IN COLLISIONALLY INDUCED FLUORESCENCE
H. HARKER, A.J. ROSS, T. BERGEMAN

H30 – H-BOND TOPOLOGY IN THE TRIFLUOROETHANOL TRIMER
JAVIX THOMAS, WOLFGANG JÄGER, YUNJIE XU

H31 – SPECTROSCOPIC IDENTIFICATION OF α,α-DICHLOROBENZYL RADICAL FROM CORONA DISCHARGE OF BENZOTRICHLORIDE
YOUNG WOOK YOON and SANG KUK LEE

H32 – FOURIER TRANSFORM 12CH3D SPECTRA IN THE REGION 3800 – 8000 cm–1. DIRECT COMPARISON TO AB INITIO CALCULATION
L. DAUMONT, X. THOMAS, M. REY, B. GROUIEZ, G. ALBORA, L. REGALIA, V. TYUTEREV, A. V. NIKITIN

H33 – PRESENT STATUS AND PERSPECTIVES OF LINE-BY-LINE ANALYSES OF THE PH3 ABSORPTION SPECTRUM IN THE OCTAD RANGE BETWEEN 2800 AND 3600 cm–1
A. V. NIKITIN, Y. A. IVANOVA, M. REY, V.I.G. TYUTEREV, L.R. BROWN

H34 – HIGH-PRECISION CAVITY RING-DOWN SPECTROSCOPY OF THE MOLECULAR OXYGEN a1Δg ← X3Σg BAND
J. T. HODGES, V. T. SIROUNEAU, A. J. FLEISHER, D. A. LONG

Invited Lectures I, Wednesday, August 26, 9:00

Chair : M. ROTGER

I1 – ENANTIOMER DIFFERENTIATION USING BROADBAND ROTATIONAL SPECTROSCOPY (45 min.)
MELANIE SCHNELL

I2 – PROBING DYNAMICS VIA HIGH RESOLUTION INFRARED SPECTROSCOPY: FROM INTERSTELLAR HYDROCARBON RADICALS TO COLLISIONS AT GAS-LIQUID INTERFACES (45 min.)
D. J. NESBITT
Invited Lectures J, Wednesday, August 26, 11:00

Chair: D. BERMEJO

J1 – THE HYDRATION STRUCTURE OF AQUEOUS CARBONIC ACID AND CARBON DIOXIDE FROM X-RAY ABSORPTION SPECTROSCOPY (45 min.)
R. J. SAYKALLY

J2 – LINE SHAPE PARAMETERS FOR MOLECULES OBSERVED IN PLANETARY ATMOSPHERES (45 min.)
R. GAMACHE

Invited Lectures K, Thursday, August 27, 9:00, Mini-Symposium, Excitons, interatomic Coulomb decay, and dipole-dipole interactions

Chair: F. MERKT

K1 – ICD AND ITS EXPLORATION BY SHORT, INTENSE AND COHERENT LIGHT PULSES (30 min.)
LORENZ S. CEDERBAUM

K2 – STATE RESOLVED UV STUDIES OF FLEXIBLE BICHROMOPHORES (30 min.)
DAVID F. PLUSQUELLIC, TIMOTHY S. ZWIER

K3 – EXOTIC CHEMISTRY WITH ULTRACOLD RYDBERG ATOMS (30 min.)
JOHANNES DEIGLMAYR

Poster Session L, Thursday, August 27, 11:00

L1 – ADDITION TO THE HITRAN DATABASE OF LINE-SHAPE PARAMETERS DUE TO THE PRESSURE OF H₂, HE and CO₂. PART I: SO₂, NH₃, HF, HCL, OCS and C₂H₂
J. S. WILZEWSKI, I. E. GORDON, R. V. KOCHANOV, C. HILL, L. S. ROTHMAN

L2 – EXPERIMENTAL AND THEORETICAL STUDY OF N₂-PRESSURE-INDUCED LINE-SHAPE PARAMETERS IN THE v₃ AND v₅ BANDS OF CH₃D
V.M. DEVI, A. PREDOL-CROSS, K. SUNG, T. SINYAKOVA, J. BULDYREVA, D.C. BENNER, M.A.H. SMITH, A. MANTZ

L3 – CRDS ABSORPTION SPECTRUM OF NATURAL WATER VAPOUR BETWEEN 7911 AND 8337 CM⁻¹
A. CAMPARGUE, B. GUILLO LOHAN, D. MONDELAIN, S. KASSI, E.V. KARLOVETS, S.N. MIKHAILENKO

L4 – CRDS ABSORPTION SPECTRUM OF ¹⁷O WATER VAPOUR BETWEEN 5850 AND 6670 CM⁻¹
S.N. MIKHAILENKO, A. CAMPARGUE, D. MONDELAIN, S. KASSI, O. LESHCHISHINA, E.V. KARLOVETS

L5 – MILLIMETERWAVE SPECTROSCOPY OF ETHANIMINE AND PROPANIMINE AND THEIR SEARCH IN ORION
L. MARGULÈS, R. A. MOTYENKO, J.-C. GUILLEMIN, J. CERNICHARO
L6 – FIRST SPECTROSCOPIC STUDIES AND DETECTION IN SgrB2 OF $^{13}$C-DOUBLY SUBSTITUED ETHYL CYANIDE
L. MARGULÈS, R. A. MOTIYENKO, J.-C. GUILLEMIN, H. S. P. MÜLLER, A. BEL-LOCHE

L7 – SYNCHROTRON-BASED HIGH RESOLUTION THz SPECTROSCOPY BETWEEN 0.8 AND 3 THz USING A COLLISIONAL COOLING MULTIREFLECTION CELL
S. ALBERT, S. BAUERECKER, I. BOLOTOVA, Ph. LERCH, M. QUACK, A. WOKAUN

L8 – METHYL INTERNAL ROTATION IN THE MICROWAVE SPECTRUM OF VINYL ACETATE
H. V. L. NGUYEN, A. JABRI, V. VAN, W. STAHL

L9 – JET-COOLED BIS(XYLENE)CHROMIUM ROTATIONAL ISOMERS STUDIED WITH HIGH-RESOLUTION LASER IONIZATION SPECTROSCOPY
S. KETKOV, E. RYCHAGOVA, S. MAKAROV, G. ZABRODINA, H. SELZLE

L10 – CLS SYNCHROTRON IR AND FIR SPECTROSCOPY OF CD$_3$OH: $r$-LADDERS AND VIBRATIONAL DRAINS IN THE METHANOL TORSIONAL BATH
R.M. LEES, LI-HONG XU, E.M. REID, J. MYSHRALL, B.E. BILLINGHURST

L11 – IMPLEMENTING PRESSURE BROADENING IN MOLECULAR LINE LISTS FOR APPLICATION TO EXTRASOLAR PLANETS

L12 – ACCURATE AB INITIO PREDICTIONS OF METHANE SPECTRA UP TO 12000 CM$^{-1}$ AT VARIOUS T-CONDITIONS
M. REY, A. V. NIKITIN, VI. G. TYUTEREV

L13 – COLLISION INDUCED BROADENING OF HFC-32 RO-VIBRATIONAL TRANSITIONS: SELF-, N$_2$- AND O$_2$- BROADENING COEFFICIENTS
N. TASINATO, A. PIETROPOLLI CHARMET, P. STOPPA, S. GIORGIANNI

L14 – A VARIATIONALLY COMPUTED LINE-LIST FOR HOT ETHYLENE
A. I. PAVLYUCHKO, S. N. YURCHENKO, J. TENNYSON

L15 – HIGH RESOLUTION INFRARED SPECTRA OF JET-COOLED DI- AND TRI-ACE-TYLENE
K.D. DONEY, D. ZHAO, H. LINNARTZ

L16 – AB INITIO STUDY OF THE CH$_4$–Ar POTENTIAL AND INDUCED DIPOLE SURFACES: TRUE BOUND DIMER AND COLLISION-INDUCED ABSORPTION
Y. N. KALUGINA, S. E. LOKSHTANOV, A. A. VIGASIN

L17 – OXYGEN B-BAND TRANSITIONS FREQUENCIES AND LINE-SHAPE PARAMETERS FOR ATMOSPHERIC APPLICATION
J. DOMYSŁAWSKA, S. WÓJTEWICZ, A. CYGAN, P. MASŁOWSKI, K. BIELSKA, P. WCIŚŁO, M. ZABOROWSKI, M. PIWIŃSKI, R. S. TRAWIŃSKI, R. CIURYŁO and D. LISAK

L18 – SUBVIBRATIONAL LIF SPECTROSCOPY OF THE $B^2 \Pi(3^3 P_1) \leftarrow X^1 \Sigma^+ (5^1 S_0)$ TRANSITION IN EXCITATION SPECTRUM OF CDNE VAN DER WAALS COMPLEX
T. URBANCZYK, J. KOPERSKI

L19 – SPECTRAL TAXONOMY: A SEMI-AUTOMATED COMBINATION OF CHIRPED-PULSE AND CAVITY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY
K. N. CRABTREE, M. A. MARTIN-DRUMEL and M. C. McCARTHY
L20 – HIGH-RESOLUTION VUV-ABSORPTION SPECTROSCOPY USING MODULATION TECHNIQUES
U. HOLLENSTEIN, H. SCHMUTZ, F. MERKT

L21 – THE TORSION AND ROTATION-TORSION SPECTRA OF DOUBLY DEUTERATED METHANOL CD2OH
M. NDAO, L. H. COUDERT, and F. KWABIA TCHAN, L. MARGULÈS and R. A. MOTYENKO, J. BARROS, L. MANCERON, P. ROY

L22 – FULL-DIMENSIONAL QUANTUM DYNAMICS AND SPECTROSCOPY OF AMMONIA ISOTOPOMERS
CSABA FÁBRI, ROBERTO MARQUARDT, MARTIN QUACK

L23 – MOL-D A DATABASE FOR PHOTO-DISSOCIATION CROSS-SECTIONS FOR INDIVIDUAL RO-VIBRATIONAL STATES OF DIATOMIC MOLECULAR IONS
D. JEVREMOVIĆ, A. A. MIHAJLOV, V. A. SREČKOVIĆ and L. M. IGNJATOVIĆ, M. S. DIMITRIJEVIĆ, V. VULJČIĆ

L24 – CHEMI-IONIZATION PROCESSES CAUSED BY THE CREATION OF QUASI-MOLECULAR COMPLEXES IN ATOM - RYDBERG ATOM COLLISIONS
A. A. MIHAJLOV and V. A. SREČKOVIĆ, M. S. DIMITRIJEVIĆ

L25 – WAVE FUNCTIONS AND LIFETIMES OF OZONE METASTABLE STATES ABOVE THE DISSOCIATION THRESHOLD : IMPACT ON THE DYNAMICS
VIATCHESLAV KOKOOLEN, DAVID LAPIERRE, ALEXANDER ALIJAH, VLADIMIR TYUTEREV, ROMAN KOCHANOV, JUAN BLANDON

L26 – HOT WATER EMISSION SPECTRA: ROTATIONAL ENERGY LEVELS OF THE (000) AND (010) STATES OF HD17O
G. CH. MELLAU, S.N. MIKHAILENKO, VL. G. TYUTEREV

L27 – IONIZATION SPECTROSCOPY AND PHOTOPHYSICS OF MOLECULES OF ASTROPHYSICAL AND BIOLOGICAL INTEREST IN THE FAR ULTRAVIOLET: THEORY AND EXPERIMENT
M. SCHWELL, Y. BENILAN, M.-C. GAZEAU, A. BELLILI, M. HOCHLAF, J.-C. GUILLEMIN, L. POISSON

L28 – THE BAND SYSTEM OF ETHANE AROUND 7 MICRON: FREQUENCY ANALYSIS OF THE ν6 BAND
N. MOAIZEN-AHMADI, J. NOROOZ OLIAE

L29 – CLASSICAL TRAJECTORY SIMULATION OF LINE MIXING EFFECTS IN ISOTROPIC RAMAN SPECTRA OF PURE NITROGEN: FROM LOW TO HIGH TEMPERATURES
SERGEY V. IVANOV

L30 – NITROGEN DIOXIDE HIGH TEMPERATURE LINE LIST IN THE 466-3374 CM−1 REGION
A. A. LUKASHEVSKAYA, V. I. PEREVALOV, A. PERRIN

L31 – LOW TEMPERATURE BROADENING COEFFICIENTS IN THE ν2 BAND OF CHLOROMETHANE
S. LEONIS, M. LEPÈRE

L32 – MAGNETIC SPIN-TORSION COUPLING IN METHANOL
E. A. ALEKSEEV, V. V. IL'YUSHIN, A. A. MESHCHERYAKOV, L. H. COUDERT

L33 – A NEW AB INITIO PES AND DMS FOR NH3
Invited Lectures M, Thursday, August 27, 14:00

Chair: B. LAVOREL

M1 – ELUCIDATING STRUCTURES OF CARBOHYDRATES BY HIGH RESOLUTION SPECTROSCOPIES (45 min.)
E. J. COCINERO

M2 – ELECTRONIC SPECTRA OF ORGANIC RADICALS AND IONS OF RELEVANCE TO INTERSTELLAR SPACE AND COMBUSTION (45 min.)
JOHN P. MAIER

Poster Session N, Thursday, August 27, 16:00

N1 – WORKING WITH THE HITRAN DATABASE USING HAPI: HITRAN APPLICATION PROGRAMMING INTERFACE
R. V. KOCHANOV, I. E. GORDON, C. HILL, L. S. ROTHMAN, J. S. WILZEWSKI, P. WCISLO

N2 – HIGH-RESOLUTION STIMULATED RAMAN SPECTROSCOPY AND ANALYSIS OF ν2 AND ν3 BANDS OF 13C2H4 USING THE D2h TOP DATA SYSTEM
A. ALKADROU, M. ROTGER, D. BERMEJO, V. BOUDON

N3 – MEASUREMENTS AND THEORETICAL MODELLING OF COLLISIONAL LINE-SHAPE PARAMETERS FOR THE ν1 + ν3 BAND OF ACETYLENE PERTURBED BY CARBON DIOXIDE
K. ESTEKI, A. AL MASHWOOD, H. ROZARIO, A. PREDOI-CROSS, A.S. DUDARENOK, N.N. LAVRENTIEVA, J. BULDYREVA

N4 – HIGH RESOLUTION ANALYSIS OF THE ETHYLENE–1–13C SPECTRUM IN THE REGION 690–1700 CM⁻¹
O. N. ULENIKOV, O. V. GROMOVA, E. S. BEKHTEREVA, Yu. S. ASLAPOVSKAYA, M. G. GABONA, T. L. TAN

N5 – HIGH RESOLUTION ANALYSIS OF THE C2H2D2-TRANS MOLECULE IN THE REGION OF 1400–2000 CM⁻¹
O. N. ULENIKOV, O. V. GROMOVA, E. S. BEKHTEREVA, A. G. LITVINOVSKAYA, YU. S. ASLAPOVSKAYA, S. BAUERECKER, C. SYDOW

N6 – FOUR YEARS OF THE EXOMOL PROJECT: MOLECULAR LINE LISTS FOR EXOPLANET AND OTHER HOT ATMOSPHERES

N7 – THE NUCLEAR SPIN CONVERSION RATE OF CH4 IN A Kr MATRIX MEASURED BY FTIR SPECTROSCOPY
T. SUGIMOTO, K. YAMAKAWA, I. ARAKAWA

N8 – FTIR SPECTROSCOPY OF D2O CLUSTERS ISOLATED IN SOLID RARE GAS MATRICES
Y. SHIMAZAKI, K. YAMAKAWA, I. ARAKAWA

N9 – DETERMINATION OF EXCITED STATE DIPOLE MOMENTS VIA ELECTRONIC STARK SPECTROSCOPY: 5-METHOXYINDOLE
W. LEO. MEERTS, J. WILKE, M. WILKE, M. SCHMITT
N10 – AN EFFICIENT ALGORITHM FOR A HIGH-PRECISION H₂ ENERGY CALCULATION WITH AN EXPONENTIALLY CORELATED BASIS
P. CZACHOROWSKI, K. PACHUCKI

N11 – GROWTH PROCESSES OF D₂O CLUSTERS IN A CH₄ MATRIX OBSERVED BY FTIR SPECTROSCOPY
N. EHARA, K. YAMAKAWA, I. ARAKAWA

N12 – NEW ACCURATE WAVE NUMBERS OF H₃⁵Cl⁺ AND H₃⁷Cl⁺ ROVIBRATIONAL TRANSITIONS IN THE ν = 1 ← 0 BAND OF THE 2Π STATE
J. L. DOMÉNECH, M. CUETO, V. J. HERRERO, I. TANARRO, J. CERNICHARO, B. DROUIN

N13 – HIGH PRESSURE CAVITY RING DOWN SPECTROSCOPY: APPLICATION TO THE ABSORPTION CONTINUUM OF CO₂ NEAR 1.7 MICRONS
S. KASSI, D. MONDELAIN, A. CAMPARGUE, H. TRAN

N14 – FT EMISSION SPECTRA OF THE DEUTERATED AND ¹⁷O ENRICHED WATER BETWEEN 320 AND 550 CM⁻¹
S.N. MIKHAILENKO, O.V. NAUMENKO, G. CH. MELLAU

N15 – THE WATER DIMER INVESTIGATED IN THE 2OH OVERTONE RANGE USING CAVITY-RING DOWN SPECTROSCOPY
N. SUAS-DAVID*, R. GEORGES, T. VANFLETEREN*, T. FÖLDES, M. HERMAN, S. KASSI

N16 – MICROWAVE SPECTROSCOPY OF CAMPHENE
E. M. NEEMAN, P. DRÉAN, T. R. HUET

G.CH. MELLAU, A.A. KYUBERIS, N. ZOBOV, O.L. POLYANSKY, R.W. FIELD

G.CH. MELLAU, A.A. KYUBERIS, N. ZOBOV, O.L. POLYANSKY, R.W. FIELD

N19 – ELECTRONIC STATES OF Rb₂. AB INITIO PREDICTIONS, AND OBSERVATION OF THE 9Σ⁺_u AND 9Π_u STATES BY POLARIZATION LABELLING SPECTROSCOPY
P. KOWALCZYK, W. JASTRUCTION, J. SZCZEKPUSKI, A.R. ALLOUCHE, P. CROZET, A.J. ROSS

N20 – DUAL-LASER ABSORPTION SPECTROSCOPY OF C₂H₂ AT 1.4 µm
E. FASCI, A. CASTRILLO, T. ODINTSOVA, M.D. DE VIZIA, L. MORETTI, L. GIANNI

N21 – SENSITIVITY OF ISOTOPIC LIH ROTATION AND ROTATION-VIBRATION TRANSITIONS TO A VARIATION OF PROTON-TO-ELECTRON MASS RATIO CONSTANT
F. L. CONSTANTIN

N22 – A NEW TREATMENT OF THE ν₄ AND 2ν₄ ROVIBRATIONAL BANDS OF PF₃ ARROUND 347 cm⁻¹ AND 693 cm⁻¹
HAMID NAJIB
N24 – STABILITY OF RO-VIBRATIONAL STATES OF H₂O, HD₂O and D₂O
V. V. MELNIKOV, S. N. YURCHENKO, P. JENSEN, O. L. POLYANSKÝ, R. I. OVSYANNIKOV

N25 – TUNNELING AND PARITY VIOLATION IN TRISULFANE (HSSSH): AN ALMOST IDEAL MOLECULE FOR DETECTING PARITY VIOLATION IN CHIRAL MOLECULES
CSABA FÁBRI, LUBOŠ HORNÝ, MARTIN QUACK

N26 – HIGH SENSITIVITY LASER SPECTROSCOPIES OF METAL HYDRIDE RADICALS: LABORATORY MEASUREMENTS FOR STELLAR SPECTROSCOPY
G. DOBREV, A. PASHOV, D. TOKARYK, P. CROZET, J. MORVILLE, A.J. ROSS

N27 – 2OH OVERTONE SPECTROSCOPY OF WATER-CONTAINING VAN DER WAALS SPECIES
T. VANFLETEREN, T. FÖLDES, M. HERMAN, J. LIÉVIN, and J. LOREAU, L. H. COUDERT

N28 – UNEXPECTED VAN DER WAALS BANDS IN THE 2OH OVERTONE SPECTRA OF AMMONIA
T. VANFLETEREN, T. FÖLDES, M. HERMAN, J. LIÉVIN, L. H. COUDERT

N29 – CONVERGENCE AND ISOTOPIC STUDIES OF METHANE SPECTRA BY GLOBAL VARIATIONAL CALCULATIONS
M. REY, A. V. NIKITIN, Vl.G. TYUTEREV

N30 – AB INITIO CALCULATION OF ENERGY LEVELS AND RO-VIBRATIONAL SPECTRA FOR SiH₄ MOLECULE
A. V. NIKITIN, Y. S. CHIZHMAKOVA, M. REY, Vl.G. TYUTEREV

N31 – MQDT-ASSISTED HIGH-RESOLUTION SPECTROSCOPY OF THE RYDBERG STATES OF H₂ - IONIZATION ENERGY OF H₂ AND ROVIBRATIONAL STRUCTURE OF H⁺
M. BEYER and F. MERKT, CH. JUNGEN

N32 – THE FIRST LABORATORY OBSERVATION OF THE J = 1–0 ROTATIONAL TRANSITION OF ³⁶ArH AND ³⁸ArH
L. DORE, C. DEGLI ESPOSTI, L. BIZZOCCHI, F. TAMASSIA, E. CANÉ

N33 – PREPARATION AND SPECTROSCOPY OF ALKALI-ALKALINE EARTH DIATOMICS ON COLD HELIUM DROPLETS
F. LACKNER, J. POTOTSCHNIG, and W. E. ERNST

Poster Session O, Thursday, August 27, 20:00

O1 – THE EXPERIMENTAL EQUILIBRIUM STRUCTURE OF C₂H₂
F. TAMASSIA, E. CANÉ, L. FUSINA, G. DI LONARDO

O2 – THE INFRARED SPECTRUM OF ¹⁵NH₃ IN THE REGION 65-2000 cm⁻¹
A. PREDOI-CROSS, H. ROZARIO, E. CANÉ, L. FUSINA, G. DI LONARDO, F. TAMASSIA, M. HERMAN

O3 – FOURIER TRANSFORM SPECTROSCOPY WITH RESOLUTION BEYOND THE OPTICAL PATH LIMIT
P. MASŁOWSKI, G. KOWZAN, K. F. LEE, M. E. FERMANN, A. FOLTYNOWICZ, A. C. JOHANSSON, A. KHODABAKHSH, L. RUTKOWSKI
O4 – DISPERSED FLUORESCENCE SPECTROSCOPY OF THE SiCN $\tilde{A}^2\Delta\rightarrow\tilde{X}^2\Pi$ TRANSITION
MASARU FUKUSHIMA and TAKASHI ISHIWATA

O5 – A QUANTUM CHEMISTRY STUDY OF THE Na$_3$ GROUND STATE: TUNNELING, FINE AND HYPERFINE STRUCTURE IN A CLASSICAL JAHN-TELLER SYSTEM
A. W. HAUSER, J. POTOTSCHNIG, and W. E. ERNST

O6 – EXPERIMENTAL ROVIBRATIONAL CONSTANTS AND EQUILIBRIUM STRUCTURE OF NITROGEN TRIFLUORIDE
HAMID NAJIB

O7 – SYNCHROTRON FTIR SPECTROSCOPY OF CH$_3$SH AT THE CANADIAN LIGHT SOURCE
R.M. LEES, LI-HONG XU, E.M. REID, J.A. MYSHRALL, B.E. BILLINGHURST

O8 – VALIDATION AND EVOLUTION OF THE GEISA SPECTROSCOPIC DATABASE: A NEW APPROACH
R. ARMANTE, N. JACQUINET, N.A. SCOTT, A. CHEDIN and L. CREPEAU

O9 – AB INITIO SPECTROSCOPY FOR TRANSITION METAL DIATOMICS
L. K. MCKEMMISH, L. LODI, M. GORMAN, S. N. YURCHENKO, J. TENNYSON

O10 – GLOBAL MODELING OF HIGH-RESOLUTION SPECTRA OF ACETYLENE (C$_2$H$_2$)
O. M. LYULIN, V. I. PEREVAŁOV

O11 – ABSORPTION AND EMISSION SPECTRA OF NEUTRAL Au(NHC)X (X=Cl, Br, AND I) AND Au-NHC DOUBLE SALTS CIS/TRANS-[Au(NHC)$_2$][AuI]$, THEORETICAL STUDY
S. Y. CHEN, J. B. LIN, and A. H. H. CHANG

O12 – THEORY OF SURFACE-ENHANCED SUM-FREQUENCY GENERATION
A. H. H. CHANG and B. J. SUN, S. H. LIN

O13 – GLOBAL FREQUENCY AND INTENSITY ANALYSIS OF THE $\nu_{10}/\nu_{17}/\nu_{4}/\nu_{12}$ BANDS SYSTEM OF $^{12}$C$_2$H$_4$ AT 10 $\mu$m USING THE D$_{2h}$ TOP DATA SYSTEM
A. ALKADROU, M. ROTGER, V. BOUDON, J. VANDER AUWERA

O14 – FREQUENCY AND INTENSITY ANALYSIS OF THE 3 $\mu$m REGION OF THE ETHYLENE SPECTRUM USING THE D$_{2h}$ TOP DATA SYSTEM
M. ROTGER, M.A. LOBONO and A. ALKADROU, J. VANDER AUWERA, V. BOUDON

O15 – TUNNELING DYNAMICS OF ANILINE C$_6$H$_5$NH$_2$ STUDIED BY SYNCHROTRON-BASED HIGH RESOLUTION THz (FTIR) SPECTROSCOPY
S. ALBERT, Ph. LERCH, M. QUACK

O16 – HIGH RESOLUTION CH$_2$ AND TH$_2$ (FTIR) SPECTROSCOPY AND THEORY OF PARITY VIOLATION AND TUNNELING FOR DITHINE AS A CANDIDATE FOR MEASURING THE PARITY VIOLATING ENERGY DIFFERENCE BETWEEN ENANTIOMERS OF CHIRAL MOLECULES
S. ALBERT, I. BOLOTOVA, Z. CHEN, C. FABRI, L. HORNY, M. QUACK, G. SEYFANG, D. ZINDEL

O17 – CO$_2$ LINE STRENGTHS MEASUREMENTS IN THE 20012–00001 BAND NEAR 2 $\mu$m
J. BRUNZENDORF, V. WERWEIN, A. SERDUYKOV, O. WERHAHN and V. EBERT
O18 – ULTRAHIGH RESOLUTION MEASUREMENTS OF RO-VIBRATIONAL-TUNNELING TRANSITIONS IN NH₃: ABSOLUTE FREQUENCIES, QUADRUPOLE SPLITTINGS AND A PROOF OF PRINCIPLE EXPERIMENT TO MEASURE MOLECULAR PARITY VIOLATION
PETER DIETIKER, EDUARD MILOGLYADOV, MARTIN QUACK, ANDREAS SCHNEIDER, GEORG SEYFANG

O19 – SPECTROSCOPIC INVESTIGATION OF METHANE FORMATION UPON REDUCIBLE OXIDES AND OXYGEN ISOTOPE MOBILITY BETWEEN MINERALS AND CARBON DIOXIDE
A. KNIŽEK, M. FERUS, P. KUBELÍK and S. CIVIŠ

O20 – THE GEISA SPECTROSCOPIC DATABASE IN 2014: CONTEXT AND CONTENTS
N. JACQUINET, R. ARMANTE, L. CREPEAU, N.A. SCOTT and A. CHEDIN

O21 – REINVESTIGATION OF THE SECOND TORSIONAL BAND OF METHYLAMINE
I. GULACZYK, M. KREGLEWSKI, V. HORNEMAN

O22 – INFLUENCE OF NANOCONFINEMENT ON ROTATIONAL DEPENDENCE OF LINE HALF-WIDTHS OF CARBON OXIDE
A.A. SOLODOV, YU.N. PONOMAREV, T.M. PETROVA and A.M. SOLODOV

O23 – ANALYSES OF FOUR BANDS OF THE $^{16}$O$^{18}$O$^{18}$O ISOTOPOLOGUE OF OZONE BY CRDS IN THE 5850 – 6920 cm$^{-1}$ REGION

O24 – FTIR OZONE SPECTRA: FOCUS ON THE $^{16}$O$^{18}$O$^{18}$O C, SYMMETRY ISOTOPIC SPECIES
M-R. DE BACKER, A. BARBE, Vl. G. TYUTEREV, E. STARIKOVA

O25 – THE COMPUTATION OF SEXTIC CENTRIFUGAL DISTORTION CONSTANTS AS BENCHMARK FOR THE CUBIC FORCE FIELD OF DFT FUNCTIONALS
A. PIETROPOLLI CHARMET, P. STOPPA, N. TASINATO, S. GIORGIANNI

O26 – A CCSD(T) STUDY ON THE VIBRATIONAL SPECTRA OF R1122
A. PIETROPOLLI CHARMET, P. STOPPA, N. TASINATO, S. GIORGIANNI

O27 – HUGE QUANTUM SYMMETRY EFFECT IN THE O+O₂ EXCHANGE REACTION
G. GUILLON, R. RAJAGOPALA RAO, S. MAHAPATRA, B. BUSSERY-HONVAULT, P. HONVAULT

O28 – LINE PARAMETER CONSISTENCY STUDY OF OZONE AT 4.8 AND 10 µm USING ATMOSPHERIC FTIR SPECTRA FROM THE GROUND
YAO TÉ, PASCAL JESECK, CORINNE BOURSIER, CHRISTOF JANSSSEN

O29 – HIGH RESOLUTION ANALYSIS OF THE WEAK AND COMPLEX $v_3 + v_6 - v_4$ AND $v_3 + v_5$ BANDS OF SF₆ MOLECULE: A WAY TO ACCESS $v_3 + v_6 - v_6$ AND $v_3 + v_5 - v_5$ HOT BANDS
M. FAYE, P. ROY, L. MANCERON, V. BOUDON, M. LOËTE

O30 – COMPUTATIONAL MOLECULAR SPECTROSCOPY OF NCS IN THE $\tilde{X}$ 2Π ELECTRONIC GROUND STATE
JENS FREUND, PER JENSEN, TSUNEHO HIRANO

O31 – PRESSURE BROADENING OF THE DIPOLE AND RAMAN LINES OF CO₂ BY ARGON: STRINGENT TEST OF CLASSICAL IMPACT THEORY AT DIFFERENT TEMPERATURES
SERGEY V. IVANOV
O32 – MICROWAVE SPECTROSCOPY OF NOPINONE-WATER COMPLEXES
E. M. NEEMAN, J. R. AVILES MORENO, T. R. HUET

O33 – HIGH-RESOLUTION INFRARED SPECTROSCOPIC INVESTIGATION OF $^{15}$N-AMMONIA AROUND 1.5 MICRON
T. VANFLETEREN, T. FÖLDES, A. RIZOPOULOS, M. HERMAN, J. VANDER AUWEREA, T.P. SOFTLEY, G. DI LEONARDO, L. FUSINA

Invited Lectures P, Friday, August 28, 9:00
Chair: L. ROTHMAN

P1 – HIGHLY EXCITED MOLECULAR STATES: CHALLENGE FOR SPECTROSCOPY, DYNAMICS AND ASTROPHYSICS (45 min.)
V. TYUTEREV, M. REY, T. DELAHAYE, A. NIKITIN, S. TASHKUN, R. KOCHANOV

P2 – ACCURATE SIMULATION OF SPECTRA INVOLVING JT, PJT AND SPIN-ORBIT COUPLING (45 min.)
JOHN STANTON, LAN CHENG

Poster Session Q, Friday, August 28, 11:00

Q1 – MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES
P. Wcislo, H. Cybulski, R. Ciuryło, F. Thibault, H. Tran, F. Chaussard

Q2 – NON-VOIGT LINE-SHAPE ANALYSIS OF H$_2$ SPECTRA FOR THE HITRAN DATABASE

Q3 – FTIR SPECTRA OF AR I IN 700–7000 cm$^{-1}$ RANGE: HIGH EXCITED (RYDBERG) STATES
SVATOPLUK CVIŠ, PETR KUBLÍK, ADAM PASTOREK, EKATERINA M. ZANOZINA, LIBOR JUHA, VLADISLAV E. CHERNOV, ANASTASIA A. VORONINA

Q4 – FTIR SPECTRA OF NE I IN 700–7000 cm$^{-1}$ RANGE: RYDBERG H- AND I-STATES
SVATOPLUK CVIŠ, PETR KUBLÍK, ADAM PASTOREK, EKATERINA M. ZANOZINA, LIBOR JUHA, VLADISLAV E. CHERNOV, ANASTASIA A. VORONINA

Q5 – FORMATION OF FORMAMIDE IN HIGH-ENERGY DENSITY EVENT
M. FERUS, A. KNÍŽEK, O. IVANEK, P. KUBLÍK and S. CVIŠ

Q6 – SPECTROSCOPY OF METEORS AND METEORITES ABLATION PLASMA
M. FERUS, S. CIVIS, V. SVOBODA, P. KUBLÍK, A. KNÍŽEK, L. LENZA, E. CHATZI-THEODORIDIS, S. GORKOVÁ and J. KOUKAL

Q7 – SO$_2$ - CO$_2$ BROADENING COEFFICIENTS IN THE 9 µm REGION BY TDL SPECTROSCOPY
N. TASINATO, A. PIETROPOLLI CHARMET, P. STOPPA, S. GIORGIANNI

Q8 – VIBRATIONAL ANALYSIS, ABSORPTION CROSS SECTIONS AND QUANTUM CHEMICAL CALCULATIONS OF HFC-152a
N. TASINATO, G. CESELIN, G. SARAN, P. STOPPA, A. PIETROPOLLI CHARMET, S. GIORGIANNI
Q9 – FIRST PRINCIPLES CALCULATION OF ENERGY LEVELS AND SPECTRA FOR \( AB_4 \), \( ABC_3 \) TYPE MOLECULES
A.V. NIKITIN, B.M KRISHNA, M. REY, VI.G. TYUTEREV

Q10 – ASSIGNMENT AND MODELING OF THE SPECTRUM OF \(^{13}\)CH\(_4\) RECORDED AT 80 K BETWEEN 5853 AND 6200 CM\(^{-1}\)

Q11 – VARIATIONAL CALCULATIONS OF THE VIBRATIONAL ENERGIES AND TRANSITION MOMENTS FOR ETHYLENE USING TROVE
A. YACHMENEV, S. N. YURCHENKO, J. TENNYSON

Q12 – DEPERTURBATION ANALYSIS OF THE \( A^1\Pi \) STATE IN THE LESS-ABUNDANT \(^{12}\)C\(^{35}\)O ISOTOPologue ON THE BASIS OF INVESTIGATION OF THE \( B^1\Sigma^+ \rightarrow A^1\Pi, C^1\Pi^+ \rightarrow A^1\Pi, B^1\Sigma^+ \leftarrow X^1\Sigma^+ \), AND \( C^1\Sigma^+ \leftarrow X^1\Sigma^+ \) SYSTEMS

Q13 – LASER SPECTROSCOPY OF IRIDIUM MONOCHLORIDE
S. FORAN, A. G. ADAM, C. LINTON

Q14 – EMISSION SPECTROSCOPY OF THE \( B^2\Sigma^- \rightarrow X^2\Pi \) SYSTEM OF THE \(^{12}\)CD ISOTOPologue
M. ZACHWIEJA, W. SZAJNA, R. HAKALLA, P. KOLEK, M. OSTROWSKA-KOPEC, I. PIOTROWSKA, R. KĘPA

Q15 – FIRST HIGH RESOLUTION ANALYSIS OF THE \( \nu_{21} \) BAND OF PROPANE AT 921.4 cm\(^{-1}\): EVIDENCE OF LARGE-AMPLITUDE-MOTION TUNNELLING EFFECTS

Q16 – SPIN-ROTATION HYPERFINE SPLITTINGS AT MODERATE TO HIGH J VALUES IN METHANOL
LI-HONG XU, JON T. HOUGEN, SERGEY BELOV, G. YU GOLUBIATNIKOV, ALEXANDER LAPINOV, V. V. ILYUSHIN, E. A. ALEKSEEV, A. A. MESCHERYAKOV

Q17 – THE INTRINSIC RING-PUCKERING CONFORMATION OF AN ISOLATED RIBOFURANOSE UNIT
P. ÉCIJA, I. URIARTE, F. J. BASTERRETXEA and E. J. COCINERO, L. SPADA and W. CAMINATI, B. G. DAVIS, A. LESARRI

Q18 – HIGH RESOLUTION SPECTROSCOPY AND QUANTUM DYNAMICS OF FLUOROFORM
I. BOLOTOVA, O. ULENIKOV, E. BEKHTEREVA, S. ALBERT, H. HOLLENSTEIN, M. QUACK

Q19 – SYNCHROTRON-BASED ROTATIONAL SPECTROSCOPY BETWEEN 0.8 AND 2 THz: ANALYSES OF THE THz SPECTRA OF THE CHIRAL MOLECULES OXIRANE CARBONITRILE (CH\(_2\)OCHCN) AND METHYL OXIRANE (CH\(_2\)OCHCH\(_3\))
S. ALBERT, PH. LERCH, K. KEPPLER, M. QUACK

Q20 – TWO LINEAR CARBON MOLECULES: AB INITIO POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES OF CCC AND HCCH
K. CHUBB, R. DIAMANTOPOULOU, A. YACHMENEV, S. N. YURCHENKO, J. TENNYSON
Q21 – MOLECULAR LINE LISTS FOR SCANDIUM AND TITANIUM HYDRIDE USING THE DUO PROGRAM
L. LODI, S. N. YURCHENKO, J. TENNYSON

Q22 – THE MICROWAVE SPECTRUM OF BENZANILIDE
S. HERBERS, D. WACHSMUTH, M. K. JAHN, J.-U. GRABOW

Q23 – DIMERIZATION EQUILIBRIUM OF ACETIC ACID IN THE GAS PHASE FROM INFRARED SPECTROSCOPY AND ELECTRONIC STRUCTURE CALCULATIONS

Q24 – INTERNAL ROTATION AND QUADRUPOLE COUPLING IN \(^{14}N\)-METHYLDIACETAMIDE
K. EIBL, R. KANNENGIESSER, H. V. L. NGUYEN, W. STAHL

Q25 – HITRANONLINE: A NEW STRUCTURE AND INTERFACE FOR HITRAN LINE LISTS AND CROSS SECTIONS
C. HILL, L. S. ROTHMAN, I. E. GORDON, R. V. KOCHANOV, P. WCISLO, J. S. WILZEWSKI

Q26 – MICROWAVE SPECTROSCOPIC AND QUANTUM CHEMICAL INVESTIGATIONS ON PHENYL FORMATE AND PHENETOLE
L. FERRES, W. STAHL, H. V. L. NGUYEN

Q27 – HIGH RESOLUTION THRESHOLD IONIZATION SPECTROSCOPIC STUDY OF UNSYMMETRICAL CHROMIUM BISARENE COMPLEXES IN A SUPersonic JET
S. KETKOV, G. MARKIN, E. RYCHAGOVA, H. SEIZLE, W.-B. TZENG, S.-Y. TZENG

Q28 – CONTINUOUS MONITORING OF PHOTOLYSIS PRODUCTS BY TERAHERTZ SPECTROSCOPY
A. OMAR, A. CUISSET, G. MOURRET, F. HINDLE, S. ELIET, R. BOCQUET

Q29 – ISOLATED LINE-SHAPE OF METHANE WITH VARIOUS COLLISION PARTNERS
T. LE, L. FISSIAUX, and M. LEPÈRE, H. TRAN

Q30 – MASS-ANALYZED THRESHOLD IONIZATION SPECTROSCOPY OF JET-COOLED TRANSITION METAL CYCLOPENTADIENYL COMPLEXES
S. KETKOV, G. MARKIN, W.-B. TZENG, S.-Y. TZENG

Q31 – GLOBAL ANALYSIS OF HIGH RESOLUTION IR EMISSION SPECTRUM OF \(^{12}CH_4\) IN THE DYAD \((v_2/v_4)\) REGION
B. AMYAY, V. BOUDON, J. VANDER AUWERA, R. GEORGES, O. PIRALI

Q32 – FOURIER TRANSFORM SPECTROSCOPY AND GLOBAL DEPERTURBATION ANALYSIS OF THE \(^{1}A^1\Sigma^+\) AND \(^{3} \Pi\) STATES IN KRb MOLECULE
K. ALPS, A. KRUIZINS, M. TAMANIS, R. FERBER, E. A. PAZYUK, A. V. STOLYAROV

Q33 – ROTATIONAL SPECTROSCOPY OF TRANS-METHYLGLOXYL
S. BTEICH, M. GOUBET, R. A. MOTTIYENKO, L. MARGULÉS and T. R. HUET
Invited Lectures A

Monday, August 24, 9:00

Chair : M. HERMAN
Molecular Physics Lecture

MOLECULES IN MOTION: SYMMETRIES AND INTRAMOLECULAR PRIMARY PROCESSES BETWEEN YOCOTSECONDS AND DAYS AS DERIVED FROM HIGH RESOLUTION SPECTROSCOPY AND THEORY (45 min.)

MARTIN QUACK, ETH Zurich, Physical Chemistry, CH-8093 Zürich, Switzerland, Martin@Quack.ch

The study of the primary processes of molecular motion provides the basis for chemical reaction dynamics and kinetics. We shall start by introducing the two major experimental approaches towards intramolecular quantum dynamics and kinetics from spectra: (i) time resolved (“pump-probe”) spectroscopy, which has a long history of many decades, and (ii) deriving time dependent quantum dynamics from highly frequency resolved molecular spectra developed largely in the Zürich group over the last 3 decades. We shall then discuss the role of the successive breaking of approximate symmetries in providing an understanding of the very different time scales found for molecular primary processes. The general principles will be illustrated with results on femtosecond to nanosecond intramolecular energy flow.

1M. Quack, Molecular Physics Lecture, 24th Coll. High Resol. Molecular Spectroscopy, Dijon, August 2015
4M. Quack, “Molecules in Motion”, Chimia, 55, 753-758 (2001), see also M. Quack, “Molecular spectra, reaction dynamics, symmetries and life”, Chimia, 57, 147-160 (2003).
picosecond to nanosecond tunneling reactions \(^8\), nuclear spin symmetry conservation and violation \(^{12,13,14}\), and finally time dependent evolution of parity in chiral molecules on the timescale of milliseconds to days due to electroweak parity violation, \(^5\), \(^{15,16,17,18,19}\). If time permits we shall address some recent fundamental open problems in molecular quantum dynamics including the evolution of biomolecular homochirality in the early evolution of life\(^{19,20}\).

**Acknowledgement:** Our work is supported by ETH Zurich, Schweizerischer Nationalfonds (SNF) and the European Research Council (ERC) by an Advanced Grant and the COST action MOLIM. I am particularly indebted to my coworkers as cited in the list of references and more completely in \(^{21}\) and also represented by further papers at this meeting.

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ACCURACY IN SPECTROSCOPY (45 min.)

J. DEMAISON, Chemical Information Systems, University Ulm, Germany

Spectroscopy is believed to be highly accurate. However, when different studies are compared, the results are sometimes not compatible. Several typical examples will be given. The sources of these incompatibilities will be discussed. Diagnostics and possible remedies will be proposed.
Poster Session B

Monday, August 24, 11:00
The optical frequency comb synthesizer (OFCS) is nowadays a well established milestone for visible/near-infrared (NIR) metrology. Such a device has already found widespread application both as phase/frequency reference, thanks to its absolute traceability, and as source, thanks to its simultaneous broadband coverage and high coherence, providing unprecedented resolution, precision and sensitivity for spectroscopy. The interest in using OFCSs in the mid-infrared (MIR) region is related to applications such as trace-gas sensing with high-finesse cavities, high-precision spectroscopy and frequency metrology.

Here we present a highly-coherent MIR-comb generated through an intracavity difference frequency generation (DFG) process [1]. The 1040-nm portion of the spectrum of a visible/NIR OFCS is amplified by an Yb-doped fiber and then mixed with the intracavity radiation of a Ti:sapphire (Ti:Sa) laser in a PP-MgO:LiNbO3 non-linear crystal. A MIR-comb centered around 4330 nm is thus generated. We demonstrate that the excess frequency noise of the NIR-comb can be efficiently removed in the downconverted one by properly using a direct digital synthesis (DDS) scheme.

The MIR-comb beam has been coupled to a high-finesse cavity in order to resolve the teeth and to study the frequency noise power spectral density (FNPSD). The observed teeth are one every three because the ratio between the repetition rate of the comb and the free spectral range (FSR) of the cavity (150 MHz) is 20/3. The CO$_2$ absorption lines in air are clearly visible. We estimate an average per-tooth power of 1 $\mu$W.

In order to maximize the transmitted signal, we have thus matched $f_r$ with the following Vernier ratio:

$$f_r = \frac{20}{3} \text{FSR} = \frac{20}{3} \frac{c}{2L_0}$$

which corresponds to a given cavity length $L_0$. In this condition, the cavity selects a subset of comb teeth (one every three) at a time, that gives rise to a
single intense peak. In order to estimate the coherence of the MIR-comb we have used the high-finesse cavity as multimode frequency-to-amplitude converter to retrieve the FNPSD of the radiation in the condition established by eq. (1). From the FNPSD we have estimated a linewidth of the comb teeth of 2.0 kHz FWHM in a 1-s timescale and 750 Hz in a 20-ms timescale. This is to our knowledge the narrowest measured linewidth of a MIR-comb. Taking into account the MIR-comb power, we calculate a per-tooth power spectral density of 0.5 µW/kHz (in a 1-s timescale), which is comparable with the best values obtained with OPO-based MIR-combs [2]. It is worth noting that this power level is in a range suitable for direct comb spectroscopy in this spectral region [3].

Moreover a quantum cascade laser at 4.33 µm has been phase-locked to a comb tooth and coupled to the same cavity in order to verify its frequency narrowing: a comparison will be shown. Thanks to the locking, the QCL linewidth is reduced from about 600 kHz to 4.6 kHz in a 1-s timescale and the locking efficiency is about 73 %.

References


SUB-MILLIMETER SPECTRUM AND ASTROPHYSICAL RESEARCH OF S-METHYL THIOFORMATE

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Methyl thioformate $\text{C}_2\text{H}_4\text{OS}$, is a monosulfur derivative of methyl formate, a relatively abundant component of the interstellar medium (ISM)$^1$. S-Methyl thioformate being also the thermodynamically most stable isomer with a $\text{CH}_3\text{SC(O)H}$ formula, it can be reasonably proposed for detection in the ISM. Theoretical investigations on this molecule have been done recently by Senent et al.$^2$. Previous experimental investigations on this molecule have been performed by Jones et al.$^3$ and Caminati et al.$^4$ and its microwave spectrum was recorded between 10-41 GHz.

In this study, S-methyl thioformate has been synthesized in Rennes by reaction of methyl mercaptan on formic-acetic anhydride. The sub-millimeter spectrum was then recorded for the first time from 150 to 660 GHz with the solid-state based spectrometer in Lille.$^5$ Around 1100 lines were assigned up

to $J=55$ and $K=9$ and a global fit for ground torsional state $\nu_t=0$ performed with the BELGI-C$_6$ code of this molecule will be presented and discussed. Our aim is to provide a line list for an astrophysical research.

Carbon monoxide is present in the atmosphere of Venus \(^1\) probed by the SOIR instrument on board Venus Express, and Mars \(^2\) to be studied using the NOMAD instrument on board the ExoMars Trace Gas Orbiter. To retrieve CO concentrations from SOIR or NOMAD spectra, precise spectroscopic information on CO\(_2\) pressure broadened CO lines is required.

In this study, the absorption spectra of the 2 – 0 band of 12C\(^{16}\)O mixed with CO\(_2\) have been recorded using a Bruker IFS 120 to 125 HR upgraded Fourier transform spectrometer, at total pressures from 117 to 910 Torr and at 5 temperatures between 244 and 288 K. CO\(_2\) pressure broadening and shift coefficients, and their temperature dependences have been measured using a multi-spectrum non-linear least squares fitting technique. Various line shape models have been considered to take into account the Dicke narrowing and the speed dependent effects, including Rautian, speed dependent Voigt and speed dependent Rautian profiles. Results will be presented, compared with previous measurements \(^3\) and discussed.

\(^1\)Bertaux et al, Nature \textbf{450}, 646 (2007)
\(^2\)Krasnopolsky et al, Icarus \textbf{228}, 189 (2014)
\(^3\)Colmont et al, J Mol Spectrosc \textbf{246}, 86 (2007)
The analysis of internal rotation with low and medium barrier heights is a challenging problem in rotational spectroscopy. Especially, when more than two internal rotors are present in the molecule, the number of torsional components rapidly increases and the assignment of the spectrum becomes a difficult task. Therefore, only few molecules with three methyl rotors and, to the best of our knowledge, no four-top molecules have been studied in the microwave region so far.

Here, we present our investigations on the first molecule with four internal methyl tops: tetramethylthiophene (TMTP), a heterocyclic five-membered ring with $C_{2v}$ symmetry and two pairs of two equivalent rotors. The internal dynamics was studied by a combination of molecular beam Fourier transform microwave spectroscopy, group theory, and quantum chemistry.

The molecular symmetry group of TMTP is $G_{324}$, which may be written as the semi-direct product $(C_3 \times C_3 \times C_3 \times C_3) \times C_{2v}$. We used group theory to derive that the internal rotors in TMTP split each rotational transition in 25 torsional components and their intensities were determined by nuclear spin statistics. By a combination of four two-top fits and two three-top fits, it was possible to assign 19 of these 25 torsional species. Finally, a global four-top fit using an extended version of the XIAM code was carried out.

In previous studies on monomethyl thiophenes, intermediate barrier heights of 194 cm$^{-1}$ and 259 cm$^{-1}$ for 2-methylthiophene$^1$ and 3-methylthiophene$^2$, respectively, were found. Also 2,5-dimethylthiophene$^3$ with two equivalent tops

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3 V. Van, W. Stahl, and H.V.L. Nguyen, “Two equivalent methyl internal rotations in 2,5-dimethylthiophene investigated by microwave spectroscopy”, *to be published.*
possesses a similar barrier height of 248 cm\(^{-1}\). Surprisingly, the calculated barrier heights of TMTP at the MP2/6-311++G(d,p) level of theory were much lower (90 cm\(^{-1}\) for the 2,5-methyl tops and 160 cm\(^{-1}\) for the 3,4-methyl tops). However, B3LYP/6-311++G(d,p) level yielded much different barriers of 20 cm\(^{-1}\) and 250 cm\(^{-1}\), respectively.
To manipulate the motion of large and complex molecules or molecules in their ground state it is necessary to employ methods that are compatible with high-field-seeking states. High-field-seeking states are attracted to field maxima, which cannot be realized in free space with static fields. Therefore, motion manipulation of such states requires the use of time-dependent fields. A previous experiment using microwave fields within a resonator achieved an additional deceleration of a pre-decelerated packet of ammonia molecules\cite{Merz2013}. In this case ammonia could be considered as an isolated two-level system to a good approximation.

This experiment has now been expanded upon by using a modified experimental setup for the manipulation of a molecular beam of 4-aminobenzonitrile (ABN), a larger and heavier (118 g/mol) molecule, direct from a supersonic expansion. ABN has a large dipole moment, which is ideal for increasing the effect of the microwave fields. However, ABN also displays a more complex rotational structure than ammonia as it is an asymmetric top. Its larger density of states means that ABN cannot be treated as a two-level system. In order to predict the AC Stark shifts for the rotational energy levels of ABN we have developed a numeric program that can account for this increased complexity. Using the calculated AC Stark shifts, trajectory simulations then determine to what extent a molecular beam of ABN can be focused by our microwave resonator.

Here, we will present the results of the motion manipulation experiments carried out on ammonia as well as details of the new experimental setup and simulation results.

Acetyl- and nitrogen containing substances play an important role in chemical, physical, and especially biological systems. This applies in particular for acetamides, which contain a peptide bond (−C≡O−NH−) as a characteristic structure element. In this work, N-ethylacetamide, one of the smallest acetamides, was investigated by a combination of molecular beam Fourier transform microwave spectroscopy and quantum chemical calculations. Conformational studies on N-ethylacetamide at the MP2/6-311++G(d,p) level of theory yielded four stable minima on the potential energy surface. The most energetically favorable conformer possesses a C$_1$ symmetry and was identified in the rotational spectrum.

The $^{14}$N quadrupole hyperfine structure as well as the splittings arise from the internal rotation of the acetyl methyl group could be assigned. Due to the rather low torsional barrier of 73.4782(1) cm$^{-1}$, fine splittings are up to 4.9 GHz. The hyperfine splittings are much smaller, in the order of a few tens kHz.

The rotational constants, centrifugal distortion constants, quadrupole coupling constants, and the parameters describing the methyl torsion were determined with high accuracy using the program XIAM. The gas phase structure was confirmed not only by comparison of the experimental rotational constants to the calculated values, but also by the orientation of the internal rotor.

In order to reveal the behavior of molecules containing peptide bonds in an aqueous environment, quantum chemical calculations on N-ethylacetamide-water complexes were performed. For complexes containing one water molecule, five stable conformers were found, where the water molecule bounds to the acetyl oxygen atom in the energetically lower conformers. For complexes with

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two water molecules, eight conformers were found, where the water molecules also prefer bonding to the acetyl oxygen atom as well as a complexation as a water dimer.
Modern experimental spectroscopy now investigates extremely fluxional molecules in which all vibrational motions have amplitudes comparable in size to the linear dimensions of the molecule. In customary rovibrational theory, vibration is assumed to cause only minor distortions of the equilibrium structure, and so the molecule is viewed as a rotating, near-static system. Clearly, this theory fails for an extremely fluxional molecule. An example is protonated methane (CH$_5$)$^+$, for which customary theory fails to simulate reliably even the low-energy spectrum.

Strong intrinsic coupling of rotation and vibration precludes the usual symmetry analysis of the rovibrational states in the molecular symmetry (MS) group, as this involves initial, separate classifications of rotational and vibrational states. We show that the customary technique of equivalent rotations is applicable only for MS groups that are (isomorphic to) subgroups of SO(3), the special orthogonal group in three dimensions. To the best of our knowledge, however, the MS group of CH$_5$$^+$, $G_{240} = S_5 \otimes \{E, E^*\}$, is the first example of an MS group which is neither a subgroup of SO(3), O(3), nor SU(2). Thus, a separate symmetry classification of vibrational and rotational states becomes impossible for CH$_5$$^+$, consistent with the fact that a decoupling of vibration and rotation is impossible. We discuss the consequences of this and show that CH$_5$$^+$ represents a new class of molecules, for which usual group theoretical methods for determining selection rules and spectral assignments fail. Abandoning the ideas of customary theory, we propose a more general group theoretical treatment of extremely floppy molecules in which rotation

4 Being precise, we include its extension O(3) and the double cover group SU(2).
and vibration are considered to be inherently coupled. This potentially leads to a new combined rotation-vibration quantum number.
NEW OBSERVATIONS AND ANALYSIS OF THE EMISSION SPECTRUM OF THE $A^1\Pi \rightarrow X^1\Sigma^+$ BAND SYSTEM OF $^{12}C^{16}O$

M. OSTROWSKA-KOPEĆ, I. PIOTROWSKA, M. ZACHWIEJA, R. KĘPA, R. HAKALLA, P. KOLEK, W. SZAJNA, Materials Spectroscopy Laboratory, Department of Experimental Physics, Faculty of Mathematics and Natural Science, University of Rzeszów, 35-959 Rzeszów, Poland

In the emission spectrum of the $^{12}C^{16}O$ molecule new observations and analyses of ten bands of the fourth-positive ($A^1\Pi \rightarrow X^1\Sigma^+$) system were performed. Under high resolution and by using conventional photographic spectroscopy technique the highly excited: $6-14$, $7-15$, $7-16$, $7-17$, $7-18$, $7-19$, $8-16$, $9-21$, $10-22$ and $11-24$ bands were recorded and analysed for the first time. After detailed spectroscopic analysis the individual molecular constants and equilibrium molecular parameters of the upper $A^1\Pi$ state were calculated. The observation of five bands belonging to the $7-\nu''$ progression suggests the need of correction of relative band intensities in this group of bands$^1$. Moreover, numerous observed perturbations of the $A^1\Pi$ ($\nu = 6-11$) levels were observed and compared with so far observed as well as theoretically predicted ones$^{2,3}$.

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**SELF- AND CO₂-BROADENED LINE SHAPE PARAMETERS FOR THE ν₂ AND ν₃ BANDS OF HDO**

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Knowledge of CO₂-broadened HDO widths and their temperature dependence exponents are required to interpret atmospheric spectra of Mars and Venus. We therefore used nine high-resolution, high signal-to-noise spectra of HDO and HDO+CO₂ mixtures to obtain broadening coefficients for selected transitions of the ν₂ and ν₃ vibrational bands located at 7.13 and 2.70 µm, respectively. The gas samples were prepared by mixing equal amounts of high-purity distilled H₂O and a 99% enriched D₂O sample. Spectra at different temperatures (255-296 K) were obtained using a 20.38 cm long coolable cell installed in the sample compartment of the Bruker 125HR Fourier transform spectrometer at the Jet Propulsion Laboratory, in Pasadena, CA. The retrieved parameters included accurate line positions, intensities, self- and CO₂-broadened half-width and pressure-shift coefficients and the temperature dependences of CO₂ broadened HDO. The spectroscopic parameters for many transitions were obtained simultaneously by multispectrum fitting of all nine spectra in each band. A non-Voigt line shape with speed dependence was applied. Line mixing was also observed for several transition pairs. Preliminary results will be compared to other recent measurements reported in the literature.

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3Research described in this paper are performed at the College of William and Mary, Jet Propulsion Laboratory, California Institute of Technology, Connecticut College and NASA Langley Research Center under contracts and cooperative agreements with the National Aeronautics and Space Administration.
LINE SHAPE PARAMETERS FOR NEAR INFRARED CO$_2$ BANDS IN THE 1.61 AND 2.06 μm SPECTRAL REGIONS

V. M. DEVI, D. C. BENNER, Department of Physics, College of William and Mary, Williamsburg, VA; K. SUNG, L. R. BROWN, C. E. MILLER, T. J. CRAWFORD, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA; A. W. MANTZ, Department of Physics, Astronomy and Geophysics, Connecticut College, New London, CT; M. A. H. SMITH, Science Directorate, NASA Langley Research Center, Hampton, VA

Accurate spectroscopic measurements of self- and air-broadened Lorentz half-width and pressure-shift coefficients and their temperature dependence exponents are crucial for the Orbiting Carbon Observatory (OCO-2) mission. We therefore analyzed 73 high-resolution high signal-to-noise spectra of CO$_2$ and CO$_2$+air for OCO-2 channels at 1.61 and 2.06 μm. These spectra were recorded at various spectral resolutions (0.004-0.013 cm$^{-1}$) using two spectrometers (the Kitt Peak FTS in Arizona and the Bruker 125HR FTS at the Jet Propulsion Laboratory in Pasadena, California). Six different absorption cells with path lengths between 0.2 and 121 m were used with gas samples at a range of temperatures (170-297 K). The gas pressures ranged from 0.3-898 Torr for pure sample and 26-924 Torr for mixtures of CO$_2$ and air with CO$_2$ volume mixing ratios between 0.01 and 0.4. The cold sample spectra were acquired using a short 0.2038 m straight pass cell and a multipass Herriott cell having a 20.941 m total path. A multispectrum fitting technique was employed to fit all the spectra simultaneously with a non-Voigt line shape profile including speed dependence and full line mixing. Examples of fitted spectra and retrieved parameters in both CO$_2$ band regions will be shown. Comparisons of some of the results with other published values will be provided.

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5. Research described in this paper are performed at the College of William and Mary, Jet Propulsion Laboratory, California Institute of Technology, NASA Langley Research Center and Connecticut College under contracts and cooperative agreements with the National Aeronautics and Space Administration.
In this poster, we present the Automated Spectral Assignment Procedure (ASAP), a largely automated approach which enables fast and straightforward analysis of high-resolution rotation-vibration spectra when the rotational energy levels of one of the two vibrational states (the “reference” state) is precisely characterized¹.

A central tenet of this approach is that, all transitions that share the same rotational energy level in the less well characterized “target” state will be shifted by the same “offset” with respect to their predicted frequency: the error on the energy of the target state. By multiplying the individual spectra close to these predicted frequencies, the resulting cross-correlation plot exhibits a strong peak at the offset frequency. A real strength of this method is that because all transitions are correlated in the same way (i.e. offset frequency), the cross-correlation plot has a non-zero intensity at this position, whereas the probability of non-zero intensity at any other offset in the plot decreases rapidly with the number of predicted transitions, i.e. with the number of spectra multiplied together.

At present, the ASAP software, written in python language, allows:

- A display of the cross-correlation spectra in a similar fashion to a Loomis-Wood analysis;
- Assignment of the target state energy levels using automated peak detection;
- Export of the energy levels in Pickett’s format for subsequent non-linear least-squares fitting.

The use of the procedure, its advantages and limitations, will be illustrated by the recent studies of the vibrational spectrum of $\text{S}_2\text{O}$.

THE SOLEIL VIEW ON SULFUR RICH OXIDES:  
THE $S_2O$ BENDING ($\nu_2$) AND S–S STRETCHING ($\nu_3$) MODES  
AND THEIR ANALYSIS USING ASAP

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O. ZINGSHEIM, T. SALOMON, F. LEWEN, S. SCHLEMMER  
and S. THORWIRTH, I. Physikalisches Institut, Universität zu Köln,  
Köln, Germany

The fundamental vibrational bending ($\nu_2 \sim 380$ cm$^{-1}$) and S–S stretching  
($\nu_3 \sim 679$ cm$^{-1}$) modes of disulfur monoxide, $S_2O$, and their associated hot  
bands $2\nu_2 - \nu_2$ and $\nu_3 + \nu_2 - \nu_2$, have been observed at high spectral resolution  
at the SOLEIL synchrotron facility using Fourier-transform far-infrared spectroscopy.  
This transient species has been produced in a radio-frequency discharge by flowing SO$_2$ over elemental sulfur.  
The spectroscopic analysis has been performed using an Automated Spectral Assignment Procedure (ASAP)  
which has enabled an accurate determination of the energy levels of the observed vibrational states.$^1$

In addition to the high-resolution synchrotron study, pure rotational spectra  
of $S_2O$ in the $v_2 = 1$, $v_2 = 2$, and $v_3 = 1$ vibrational states were observed in  
the frequency range 250 – 500 GHz by absorption spectroscopy in a long-path absorption cell.  
From these combined measurements, extensive molecular parameter sets have  
been determined and highly accurate vibrational band centers (to better than  
$10^{-5}$ cm$^{-1}$) have been derived.

$^1$M. A. Martin-Drumel et al., The SOLEIL view on sulfur rich oxides: The $S_2O$ bending  
mode $\nu_2$ at 380 cm$^{-1}$ and its analysis using an Automated Spectral Assignment Procedure  
Protonation of methane, CH$_4$, a rather rigid molecule well-described by quantum mechanics, produces CH$_5^+$, a prototypical floppy molecule which up to now has eluded definitive spectroscopic description $^1$. Experimental measurement of high-resolution spectra of pure CH$_5^+$ samples poses a formidable challenge. By applying two types of action spectroscopy, laser induced reaction (LIR) with CO$_2$ and laser induced inhibition of helium cluster growth (LIICG), we present here low temperature high-resolution spectra of mass-selected CH$_5^+$ $^2$. A frequency comb system has been used for calibration of the frequency axis. Based on the resulting high accuracy of the line positions, we determined a spectrum of combination differences. Analysis of this spectrum enabled derivation of equally accurate ground state level schemes and to distinguish different nuclear spin isomers of this enfant terrible of molecular spectroscopy.

AN ANALYTICAL MODEL OF THE DETECTION BANDWIDTH INFLUENCE ON ABSORPTION FREQUENCY AND LINEWIDTH MEASUREMENTS

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In recent years, there has been a growing interest toward precise and accurate observations of spectral line shapes, for the purpose of either applications (atmospheric sounding, chemical analysis in the gas phase, ...) or fundamental studies (molecular collisions and line shape analysis, fundamental metrology, Doppler broadening thermometry, ...). The latter studies require a careful error budget. Surprisingly, the influence of the finite detection bandwidth has not been considered in details until very recently.

In a recent paper, a theoretical model of the influence of the detection bandwidth properties on observed line shapes has been described in the case of a continuous sweeping of the laser frequency. This model leads to an analytical form of the line shape that highlights consequences on the retrieval of the line center frequency and broadening parameters.

An analytical extension of this model to the case of a step-by-step sweeping of the laser frequency will be presented. It takes into account detection filter properties, magnitude and duration of each laser frequency step. It can also include non-Voigt line shape models, Beer-Lambert law, finite bandwidth of the laser, as well as the case of a frequency modulated laser beam.

These models have been accurately validated thanks to spectra of NH$_3$ and H$_2$O recorded with laser spectrometers in Paris-13 and Naples-2 universities under conditions chosen to enhance impact of the detection bandwidth on recorded spectra. Resulting frequency shifts and line shape distortions were perfectly taken into account by the model, leading to parameters in agreement with experiments designed to make the impact of the detection bandwidth negligible. Finally, consequences on frequency and Doppler width measurements will be discussed.

CONFORMATIONAL MAP OF THE ANESTHETIC ENFLURANE

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Following previous results on the volatile anesthetics sevoflurane,1 isoflurane2 and desflurane,3 we have analyzed the structural properties of enflurane (C-HClF-CF2-O-CHF2) using microwave spectroscopy and ab initio calculations. We detected three distinct molecular conformations (nine isotopologues), reporting here the rotational parameters and the full nuclear quadrupole coupling tensor for the observed species. Unlike the anti carbon chain in the isotructural molecule of isoflurane, the enflurane skeleton is trans. The three conformations arise from the internal rotation of the terminal chlorofluoro methyl group, adopting three alternative staggered orientations. The spectral intensities suggest a conformational composition of ca. 1:1:1, in agreement with theoretical calculations predicting very close relative energies (< 1 kJ mol⁻¹) between the three most stable species. Conformational energies were calculated up to the CCSD(T) computational level.

LINE LIST OF \( ^{15}\text{NH}_3 \) IN THE RANGE 6369 TO 6578 CM\(^{-1} \) AT ROOM TEMPERATURE

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Ammonia is a molecule observable in the atmosphere of the giant planets of the solar system. It was the first polyatomic interstellar species discovered in the field of astronomy. The measurement of isotopic ratio \( ^{14}\text{N}/^{15}\text{N} \) for this molecule is interesting for various fields. This molecule presents a large number of absorption lines in the near infrared around 1.5 \( \mu \)m. These transitions have been measured and partially assigned for the main isotopologue \( ^{14}\text{NH}_3 \).\(^1 \) Regarding to the isotopologue \( ^{15}\text{NH}_3 \), less information is available. Recently, the spectrum of \( ^{15}\text{NH}_3 \) in near infrared was investigated by Lees et al\(^2\)\(^3\)\(^4\). Assignment of some \( \nu_1 + \nu_3 \), \( \nu_1 + 2\nu_4 \) and \( \nu_3 + 2\nu_4 \) combination bands transitions have been reported but no intensities were provided. Few line positions and line strengths of \( ^{15}\text{NH}_3 \) were measured by Lins et al\(^5\), in order to find candidates for retrieving isotopic ratio of ammonia.

In this work, the spectra of \( ^{15}\text{NH}_3 \) have been recorded with an External Cavity Diode Tunable Laser Spectrometer (ECDLS) from 1520 to 1570 nm (6367-6578 cm\(^{-1} \)) at room temperature. The spectra have been calibrated and each transition fitted to Voigt profile. The recording of \( ^{14}\text{NH}_3 \) spectra helps to undoubtly attribute each transition either to \( ^{15}\text{NH}_3 \) or to \( ^{14}\text{NH}_3 \) species. A list of 2545 line positions and line strengths is presented for this isotopologue. Temperature dependence of the spectra has been studied to derive information on the lower state energy of the transitions. Finally, assignments are in progress with the help of available theoretical calculations\(^6\).

EMPIRICAL POTENTIAL ENERGY SURFACES FOR THE ELECTRONIC GROUND STATES OF BeOH, C$_3$, AND HCO$^+$

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To simulate molecular spectra we require an analytical, parameterized representation of the potential energy surface (PES) for the particular electronic state of the molecule under study. The PES parameter values can be obtained by least-squares fits of (1) ab initio energies or (2) experimentally derived rovibronic energy spacings. The experimental data are mostly too limited for the determination of a PES, so we normally use Method (1) to determine initial parameter values and then refine these by Method (2). Often, the experimental information is too limited even for the refinement. We then fit simultaneously the experimental and the ab initio energies with an appropriate weighting of the two data types. This procedure was first implemented in the program TROVE, which simulates rovibronic spectra for any molecule in an isolated electronic state, and then (as MORBID requires significantly less computer resources than TROVE for doing the same calculation) in the older program MORBID applicable to triatomic molecules only.

We are presently applying the extended MORBID program to obtain PESs for the electronic ground states of BeOH/BeOD, HCO$^+$ and C$_3$. For BeOH/BeOD, experimental data and ab initio energies are taken from Mascaritolo et al. For HCO$^+$, the experimental data are compiled by Neese and the ab initio energies are newly calculated at the core-valence RCCSD(T)/[aug-cc-pCVQZ(C, O), aug-cc-pVQZ(H)] level of theory. Finally, for C$_3$, the experimental data are compiled from diverse sources and the ab initio energies newly calculated at the CCSD(T)/aug-cc-pVQZ level of theory. Further details and results of the fits will be given at the conference.

DETECTION OF HSNO, A CRUCIAL INTERMEDIATE LINKING NO AND H₂S CHEMISTRIES

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The simplest S-nitrosothiol, thionitrous acid (HSNO), is a reactive molecule of both biological and astronomical interest. Here we report the first detection of both cis- and trans-HSNO by means of Fourier-transform microwave (FTMW) spectroscopy and microwave / millimeter-wave double resonance experiments. A precise geometrical structure determination, derived from a combination of isotopic spectroscopy and new quantum chemical calculations, yields a S–N bond of unusual length, 1.84 Å – at least 0.1 Å longer than a typical S–N bond.

Surprisingly, HSNO is readily produced when dilute mixture of gaseous H₂S and NO are simply co-expanded, i.e. without applying any discharge. Once formed, HSNO appears quite stable, as evidenced by its high steady-state concentration in our FTMW apparatus. A preliminary experimental investigation of the CH₃SH + NO reaction has recently been undertaken and we find that CH₃SNO is also formed in high abundance under similar experimental conditions.

Although calculations conclude that the reaction between H₂S, or CH₃SH, and NO is endothermic, our measurements reveal that HSNO, CH₃SNO, and possibly larger S-nitrosothiols (RSNOs), are formed with high efficiency by the reaction RSH + N₂O₃ → RSNO + HONO, where N₂O₃ is a product of NO disproportionation.
ENERGIES AND ELECTRIC PROPERTIES OF THE GROUND
AND LOW-LYING EXCITED RbCs STATES

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Reliable estimates of the energies, magnetic and electric properties of the
ground and low-lying excited diatomic states are crucial to design optimal
optical cycle for producing ultracold molecules in their absolute ground state
(v=J=0). We report here \textit{ab initio} relativistic calculations on potential energy
curves and electric properties (static dipole polarizabilities and permanent
dipole moments) of the RbCs electronic states dissociating to the ground \((5s^2S^{1/2}_1/2 (Rb) + 6s^2S^{1/2}_1/2 (Cs))\) and excited \((5s^2S^{1/2}_1/2 (Rb) + 6p^2P^{1/2,3/2}_1/2 (Cs))\) atomic states.

The assumed relativistic electronic structure model is defined by the two-
component small-core shape-consistent pseudopotentials (PPs) replacing the
inner electron shells of each atom \(^1\). These pseudopotentials were optimized
for the accurate description of the ground and low-lying excited atomic states,
emerging from the excitations of the valence s-electron of the alkali (Rb, Cs)
atom. Valence and subvalence \(((n−1)s(n−1)p)\) electrons were correlated
explicitly. Correlation calculations were performed using the two-component
spinors as one-electron basis set. The components of the spinors were expanded
in the basis of Gaussian functions. Static polarizabilities and permanent dipole
moments of the ground and excited states under study were calculated by
finite-field method. The deviations of computed energies and static dipole
polarizabilities at the dissociation limits from the relevant atomic values do
not exceed 0.8\% and 3.5\%, respectively. The obtained data will be utilized to
estimate the energies and electric properties of the fully mixed levels of the
RbCs molecule located near the second dissociation limit \(^2, 3\).

The calculations were performed with the DIRAC12 package. The present
work was supported by the RFBR under Grant No. 13-03-00466.

\(^2\) doi: 10.1103/PhysRevLett.92.153001, A. J. Kerman, J. M. Sage, S. Sainis, T. Bergeman,
\(^3\) doi: 10.1063/1.4901327, A. Kruzins, K. Alps, O. Docenko, I. Klincare, M. Tamanis,
Among other isomers of pyridinecarboxylic acid, namely, nicotinic (vitamin B3) and isonicotinic acids, picolinic acid is of great interest due to its biological properties. According to results of B3LYP/cc-pVTZ and MP2/cc-pVTZ calculations, the most stable conformer of picolinic acid (see Fig. 1a) has a planar configuration (Cs total symmetry) with antiperiplanar N–C–C=O and H–O–C=O fragments. The second conformer with a synperiplanar H–O–C=O fragment (Fig. 1b) is predicted to exist in negligible amount of ≈2% at the experimental temperature of 375 K. In comparison to the less stable conformers, the main conformer is stabilized by the OH...N hydrogen bond with $r_e(\text{N}...\text{H})=1.949$ Å(MP2/cc-pVTZ). The best ab initio structures of the lowest-energy conformers have been estimated at the CCSD(T)(ae)/cc-pwCVTZ level with extrapolation to the complete basis set limit at the MP2 level. Although the substitution structure ($r_s$) of the main conformer is already determined, the semiexperimental equilibrium structure ($r_{se}$) is still not known. In our study, the $r_{se}$ structural parameters are derived from the gas electron diffraction (GED) data taking into account vibrational corrections calculated from the MP2/cc-pVTZ harmonic and anharmonic force constants. The best estimated ab initio (CCSD(T)-based) and semiexperimental equilibrium structures are very close to each other.

Fig. 1. The most stable conformers of picolinic acid
Poster Session B, Monday, August 24, 11:00 – B21

LOW-TEMPERATURE COLLISIONAL BROADENING IN THE FAR-IR CENTRIFUGAL DISTORTION SPECTRUM OF CH₄

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Previously, we could record on the AILES Beamline at the SOLEIL Synchrotron facility the first resolved centrifugal distortion spectrum of methane (CH₄) in the THz region, which led to a precise determination of line intensities¹. Later, we could measure collisional self- and N₂-broadening coefficients at room temperature². We now reinvestigate this topic by measuring these broadening coefficients at low temperature (120 K to 160 K) for J = 5 to 12, thanks to a cryogenic multipass cell³. We used a 93 m total optical path length. Five pure methane pressures (from 10 to 100 mbar) and four CH₄/N₂ mixtures (20 % of methane, total pressure from 100 to 800 mbar) were used. These measurements allow us to obtain data for physical conditions approaching those of Titan’s atmosphere and to estimate temperature exponents.

The $R(6)$ and $R(7)$ line clusters under different pressure and gas mixture conditions.
ROTATIONAL STUDY OF THE CH$_4$–CO VAN DER WAALS COMPLEX IN THE MILLIMETER-WAVE RANGE

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In the present work, two new rotational subbands of the CH$_4$–CO van der Waals complex were detected using the intracavity OROTRON jet spectrometer in the frequency range of 114-144 GHz. The observed and assigned transitions belong to the $P$-branch of the $K = 2 - 1$ subband, correlating with internal rotor state of free methane $j_M = 0$ ($A$ symmetry) and $R$-branches of the $K = 2 - 1$ and $K = 0 - 1$ subbands, correlating with internal rotor state of free methane $j_M = 2$ ($E$ symmetry). New data sets were analyzed together with known microwave$^1$ and millimeter-wave$^{2,3}$ transitions in order to determine the molecular parameters of the CH$_4$–CO complex. The observed millimeter-wave spectrum shows numerous additional transitions which very likely belong to CH$_4$–CO, composed of methane in the $j_M = 1$ ($F$ symmetry) and $j_M = 2$ ($E$ symmetry) rotational states. Their assignments based on high quality ab initio calculations$^4$ are in progress.

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LARGE AMPLITUDE MOTION IN DIPHENYL ETHER

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The large amplitude motion of diphenyl ether in the vibronic ground state is investigated with microwave spectroscopy. At lower frequencies (2-7 GHz) rotational transitions are split into three components (I-III), a fourth component (IV) emerges at higher frequencies. Components I-III can be individually fit to an asymmetric rotor Hamiltonian to a reasonable precision, although perturbations are observed for $K_a = 2 - 3$. The fourth component appears to be more severely perturbed with a large $J$ dependence.

The flexibility of this molecule arises from the ether linkage and can be described by the two dihedral angles through this bond ($\phi_1$ and $\phi_2$). The global minimum structure, the 'twist' conformer, has $\phi_1 = \phi_2 \simeq 41^\circ$. Within a full $360^\circ$ rotation about both dihedrals there are four equivalent minima with $\phi_1 = \phi_2$. Each are separated by equivalent transition state structures in the 'skew' conformer $\phi_1 = 0^\circ$, $\phi_2 = 90^\circ$. The energy barrier between equivalent minima is approximately 1 kJ/mol. It is suspected that a tunnelling pathway involving the concerted motion of both phenyl rings exists through this potential well. A possible Coriolis interaction with a low lying ($\simeq 16 \text{ cm}^{-1}$) torsional mode is also discussed.
The infrared spectra of atomic oxygen in the range 800-13000 cm\(^{-1}\) have been investigated using the time-resolved Fourier transform spectrometric method developed in J. Heyrovský UFCH\(^1\). Atomic oxygen has been attracting the high interest of spectroscopists for many years. It is necessary to obtain detailed structure information of atomic oxygen because it plays an important role in different spectroscopic studies including the models of the atmospheres (both terrestrial and stellar) and the interstellar medium.

Up to now, the most comprehensive analysis of O I spectra were made a long time ago by Moore\(^2\), K. B. S. Eriksson and H. B. S. Isberg \(^3\), P. R. Brown, P. B. Davies and S. A. Johnson \(^4\), but most of these studies were based on ultraviolet and visible spectra, so new measurements in the infrared region can be useful to improve the data on O I levels.

The present work reports the measurement of these transitions in the range 800-13000 cm\(^{-1}\) at high resolution of 0.017 cm\(^{-1}\). From the recorded spectra we extract the energies of 5\(g\), 6\(g\), 6\(h\) and 7\(h\) levels. In addition we corrected the energy of 5\(p\) 5\(P\) state, for which Moore reports a value shifted by more than 1 cm\(^{-1}\).

Based on these measurements, we report wavenumbers of 82 lines of O I not listed in the available databases. The identification of unknown lines was achieved by calculating relative values of the transition intensities in the quantum defect approximation.

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FIRST ORDER STARK EFFECT AND TORSIONAL MOTION INTERACTION IN H$_2$O$_2$

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Terahertz pulses with an electric field amplitude on the order of 2 MV/cm can now be produced\(^1\) and can be used for coherently manipulating molecular systems. It is thus necessary to understand molecular Stark effect for such high values of the electric field. Although the interaction of an electric field with molecular motions has been thoroughly investigated in the case of rigid molecules,\(^2\) fewer results are available in the case of non-rigid molecules. The case of non-rigid molecules interacting with the electric field through first order Stark effect has been investigated by Parker *et al.*\(^3\) but the overall molecular rotation was not treated; the case of non-rigid biphenyl like molecules interacting with the electric field through second order Stark effect has been investigated treating simultaneously the large amplitude torsional motion and the overall molecular rotation.\(^4\) In the present poster the interaction of a static electric field with molecular motions will be investigated in the case of the non-rigid H$_2$O$_2$ molecule displaying a dipole moment, strongly coupled to the large amplitude torsional motion, giving rise to first order Stark effect. This large amplitude motion and the overall rotation will be both treated simultaneously.

The H$_2$O$_2$ molecule being of atmospheric interest, its high-resolution spectrum has already been studied\(^5\) and the effects of its large amplitude torsional motion are well understood.\(^6\) In the poster, the calculation of its Stark-rotation-torsion energy levels with the help of a double-valued torsional coordinate $\gamma$ parameterizing a reference configuration retrieved through *ab initio* calculations will be presented. A static electric field parallel to the laboratory fixed $Z$-axis will be assumed. The expectation value of several operators including the direction cosines $\mathbf{i}_Z \cdot \mathbf{i}_\alpha$, with $\alpha = x, y, z$, their values squared, and $\cos 2\gamma$ will be evaluated in order to understand molecular orientation/alignment and the variation of the torsional function with increasing strength of the electric field. These effects will be evaluated for a few selected levels and for an ensemble of molecules assuming a Boltzmannian equilibrium.

HIGH-RESOLUTION STUDY OF THE ROVIBRATIONAL SPECTRUM OF PF₃ IN THE 350 AND 690 cm⁻¹ REGIONS: NEW SOLUTIONS FOR OLD TOPICS

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The present work concludes the high-resolution study of the rovibrational spectrum of phosphorus trifluoride in the 350 and 690 cm⁻¹ regions. These regions comprise the ν₄ fundamental band (degenerate bending vibration at 347.087 cm⁻¹) and the much weaker 2ν₄ bands (692.847/694.637 cm⁻¹), respectively. Several attempts of studying the ν₄=2 overtone level were already published, all of them based upon assignments of the 2ν₀₀ parallel band and the 2ν₄−2−ν₄⁻¹ hot band. The present contribution provides a necessary reassignment of the 2ν₄±2−ν₄±¹ hot band and reports on the first complete study of both sublevels of the ν₄=2 overtone level. The new infrared assignments in the ν₄=2 state were combined with accurate infrared, radiofrequency, centimeter-, millimeter- and submillimeter-wave data of the ν₄=1 level, together with rotational data in the ground vibrational state, in a simultaneous fit. The existence of resonance crossings due to a ∆k = ±1, ∆l = ±2 l-type resonance in the ν₄=1 state, which generated perturbation-allowed transitions, provided independent values of the C₄ and Cζ₄ constants. Combining these rotational transitions with the wavenumbers of the ν₄ fundamental band enabled us to determine accurately the C₀ axial ground state constant. Moreover, the assignment of a few, very weak *R_K transitions in the 2ν₄−2 overtone band and their inclusion in the global least-squares fit allowed also the first accurate experimental determination of D₀₀₄/K. The obtained results are (in cm⁻¹): C₀ = 0.159970241(29) and D₀₀₄/K = 1.80457(49)×10⁻⁷. Accurate excited state parameters of the ν₄=1

(E) and $v_4 = 2 (A_1 + E)$ vibrational states, within the $Q$, $D$ and $QD$ reductions, were also obtained in the present work, and the unitary equivalence relations were checked. Moreover, anharmonic force fields of PF$_3$ were calculated at the CCSD(T) level of theory, employing correlation-consistent basis sets of valence quadruple-zeta quality. Spectroscopic constants evaluated from these force fields were found to be in excellent agreement with the corresponding experimental values.
INFRARED CROSS-SECTIONS OF NITRO-DERIVATIVE VAPORS: NEW SPECTROSCOPIC SIGNATURES OF EXPLOSIVE TAGGANTS AND DEGRADATION PRODUCTS

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Classical explosives such as RDX or TNT exhibit a very low vapor pressure at room temperature and their detection in air requires very sensitive techniques with levels usually better than 1 ppb. To overcome this difficulty, it is not the explosive itself which is detected, but another compound more volatile present in the explosive\(^1\). This volatile compound can exist naturally in the explosive due to the manufacturing process. For example, in the case of DiNitroToluene (DNT), the molecule is a degradation product of TNT and is required for its manufacture. Ortho-Mononitrotoluene (2-NT) and para-mononitrotoluene (4-NT) can be also used as detection taggants for explosive detection.

In this study, using the exceptional properties of the SOLEIL synchrotron source, and adapted multipass-cells, gas phase Far-IR rovibrational spectra of different isomers of mononitrotoluene and dinitrotoluene have been investigated. Room temperature Far-IR cross-sections of the 3 isomer forms of mononitrotoluene have been determined for the lowest frequency vibrational bands located below 700 cm\(^{-1}\)\(^2\). Cross sections and their temperature dependences have been also measured in the Mid-IR using conventional FTIR spectroscopy probing the nitro-derivatives vapors in a heated multipass-cell.


AB INITIO CALCULATION OF ENERGY LEVELS AND RO-VIBRATIONAL SPECTRA FOR GeH₄ MOLECULE

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Preliminary potential energy surface (PES) and dipole moment surfaces (DMS) of molecule GeH₄ are constructed using extended ab initio CCSD(T) calculations at 19882 nuclear configurations. The PES and DMS analytical representation are determined through an expansion in symmetry adapted products of internal nonlinear coordinates involving 282 and 692 parameters up to the 8th order and 6th order. The PES and DMS precision are discussed. Lower vibrational and rovibrational levels are calculated and compared with observed values.

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THE VIBRATIONAL SPECTRA OF 1-CHLORO-1,1-DIFLUOROETHANE (HCFC-142b) INVESTIGATED BY A COMBINED EXPERIMENTAL AND COMPUTATIONAL APPROACH

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1-Chloro-1,1-difluoroethane (HCFC-142b) is among the most employed hydrochlorofluorocarbon replacements proposed since the definite phase out of fully fluorinated chlorofluorocarbons (CFCs). Recently its atmospheric trend was obtained by the analysis of Atmospheric Chemistry Experiment (ACE) solar occultation spectra,¹ and its temperature-dependent absorption cross sections were determined up to 3500 cm⁻¹.² In the present contribution we report on the preliminary results of a combined experimental and computational investigation coupled to the accurate determination of absorption cross section data aimed to obtain a complete and reliable spectroscopic analysis up to 6500 cm⁻¹. The vibrational assignments were guided and supported by high-level calculations, where the harmonic data, obtained by means of a composite scheme that accounts for basis set truncation and core-correlation effects on top of CCSD(T)/cc-pVTZ, were combined with double-hybrid DFT (B2PLYP/maug-cc-pVTZ) cubic and semidiagonal quartic force constants, and quadratic and semidiagonal cubic electric dipole contributions to include anharmonicity on frequencies and intensities, respectively. Details of the experimental work and of the ab initio calculations are discussed together with the preliminary results.

HIGH RESOLUTION INFRARED SPECTRUM AND EQUILIBRIUM STRUCTURE OF BF₂OH

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The high-resolution Fourier transform infrared spectrum of $^{11}$BF₂OH is reanalyzed taking into account numerous interactions. In particular, the $\nu_1$, $\nu_2$, and $\nu_3$ infrared bands are analyzed for the first time and the parameters of the $6^1$, $7^1$, $8^1$, $9^1$ states and for the $4^1$ and $9^2$ interacting states are redetermined. These results are used to check the quality of the ab initio force field. It is found that the ab initio rovibrational correction is more accurate than the experimental one. An earlier attempt to determine a semiexperimental structure did not allow us to obtain an accurate equilibrium structure. The reasons of this failure are investigated. The main reason is the lack of useful experimental information. Indeed, there is no isotopic substitution available for the fluorine atoms and the boron atom is extremely close to the center of mass. Furthermore, the available isotopic substitutions ($\text{H} \to \text{D}$ and $^{16}$O $\to$ $^{18}$O) induce a large rotation of the principal axis system which amplifies the errors. However, the mixed estimation method has allowed us to determine a complete and reliable equilibrium structure.
Recent developments in optical metrology have enabled significant improvements in the accuracy and precision of the horizontal frequency axis of measured spectra. However, the precision of the vertical axis (absorption) is typically related to light intensity measurements which are prone to instrumental errors. Here we present a novel frequency-based spectroscopic technique, called one-dimensional cavity-mode dispersion spectroscopy (1D-CMDS). An important feature of the 1D-CMDS is that it provides complete information about the dispersive properties of the spectrum only by measurements of the frequencies of high-finesse cavity modes. The feasibility of frequency-based measurements of dispersion spectra was mentioned in earlier paper. However, no experimental realization was presented there. It should be emphasized that the 1D-CMDS technique depends solely on the measurement of frequencies (absolute or relative): the physical quantity that can be measured the best. This attribute gives the 1D-CMDS the potential to become the most accurate spectroscopic technique. Furthermore, because this technique yields dispersion spectra (which are more sensitive to the choice of line-shape model than absorption one), the 1D-CMDS can be used to verify the consequences of various physical effects affecting the line shape.

We present line-shape measurements of CO transition near 1.61 µm and demonstrate sub-Hz relative precision in the measurements of relative positions of cavity modes. Moreover, we compare the 1D-CMDS technique to two other high-precision cavity-enhanced spectroscopy methods: frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) and cavity mode-width spectroscopy.

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These techniques are complementary since CRDS and CMWS techniques achieve their best accuracy in different pressure ranges. In conditions of low absorption, decays of light intensity are longer and the best precision is achieved using the FS-CRDS. For higher absorption, cavity mode widths become wider, thus making the CMWS the superior technique.


MULTI-SPECTRUM ANALYSIS OF METHANE IN THE $\nu_1 + \nu_4$ AND $\nu_3 + \nu_4$ BANDS: TEMPERATURE DEPENDENCES OF SELF- AND AIR-BROADENED LINE PARAMETERS

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Methane is a trace atmospheric gas and one of most potent greenhouse gases. Due to its importance in the global Carbon Cycle, methane has received a lot of interest from both experimentalists and theoreticians alike. The management of greenhouse gases relies on the accuracies with which these gases can be measured in the terrestrial atmosphere. The spectral region located at 2.3-$\mu$m region is referred to as the methane octad. Overlapping with the methane bands are spectra of other atmospheric constituents such as CO and HF. We have measured the temperature dependencies of self- and air-broadened line parameters for transitions in the 4100 to 4500 cm$^{-1}$ spectral range. 14 high quality spectra of 99.99% $^{12}$C-enriched samples of pure methane and its dilute mixtures in dry air recorded at the Jet Propulsion Laboratory were used in this study. The spectra were recorded at temperatures between 150K and room temperature using their Bruker IFS 125 HR Fourier transform spectrometer and a gas cell with 20.38 cm built at Connecticut College that was mounted inside the Bruker instrument. Similar with previous studies, we have used a multispectrum nonlinear least-squares technique to analyze the spectra. Intercomparisons of our results with those published by other authors will be presented in our poster.

3A. Predoi-Cross and her research group was funded by NSERC, Canada. Research described in this work was performed at the College of William and Mary, Jet Propulsion Laboratory, California Institute of Technology, Connecticut College and NASA Langley Research Center under contracts and cooperative agreements with the National Aeronautics and Space Administration.
DYNAMICAL MOLECULAR STRUCTURE OF THE CO$_2$-DMS COMPLEX INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

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Some of the molecular complexes execute characteristic internal motions, as evidenced by their rotational and/or rovibrational spectra, which contain invaluable information on the motions, but are often too complicated to be readily analyzed. The CO$_2$-DMS (carbon dioxide - dimethyl sulfide) complex is a representative example of such molecular systems. Ab initio calculations show that the structure of the complex consists of the CO$_2$ lying in the plane perpendicularly bisecting the CSC plane of the DMS. One complication arises from the fact that the equilibrium conformation of the CO$_2$ slightly deviates from the $C_s$ plane of the complex, combined with a small rotation of the DMS about its symmetry axis, namely the complex is subjected to a double-minimum potential with a 1.4 cm$^{-1}$ hump at the origin. The complex is very close to a symmetric top around the energy minima, making the orientation of the $b$ and $c$ axes labile to the molecular framework, and, as the CO$_2$ rotates by the angle $\tau$ about an axis perpendicular to its molecular axis, the $B - C$ rotational constant difference increases rapidly with $\tau$. The two-fold potential barrier for the CO$_2$ is estimated to be about 140 cm$^{-1}$, much lower than 220 cm$^{-1}$ for the DMS, and in addition, because the nuclear spin of the $^{16}$O is zero, the lowest eigenstate represented by the wavefunction of the $\sum_k C_k \cos(2k\tau)$ form is separated from the first excited state of the $\sum_k S_k \sin(2k\tau)$ form by about 8 cm$^{-1}$. This is in sharp contrast with the energy level structure associated with the two-fold rotation $\theta$ of the DMS; the two lowest states $\sum_k C_k' \cos(2k\theta)$ and $\sum_k C_k'' \cos((2k+1)\theta)$ are nearly degenerate. Therefore, we expect to observe two sets of rotational spectra associated with the two lowest internal-rotation states: $\sum_k C_k \cos(2k\tau) \sum_k C_k' \cos(2k\theta)$ and $\sum_k C_k \cos(2k\tau) \sum_k C_k'' \cos((2k + 1)\theta)$. In fact, we have detected two sets of rotational spectra, each approximating the rigid-rotor pattern with quite large centrifugal corrections. The two states will interact with excited states through the Coriolis coupling and the $(B - C)\tau$ dependence extensively.
Invited Lectures C,
Mini-Symposium, New experiments with cold molecules
Monday, August 24, 14:00
Chair : Th. HUET
APPLICATIONS OF COLD MOLECULES TO FUNDAMENTAL PHYSICS (30 min.)

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Measurements using molecules can address some important unanswered questions in physics. Molecules are being used to measure the electric dipole moment (edm) of the electron, which is a sensitive test of theories that extend the Standard Model of particle physics. Those theories seek to explain such mysteries as the dominance of matter over antimatter in the Universe. Molecules are also used to search for possible variations in the fundamental constants, as hypothesized in some theories of dark energy and theories that aim to unify gravity with the other fundamental forces. Highly accurate frequency measurements may soon resolve the tiny parity-violating difference in transition frequency between the left- and right-handed enantiomers of chiral molecules. Parity-violation in nuclei is also being measured using diatomic molecules. An array of ultracold polar molecules has long-range interactions and it can be used to help understand the behaviour of quantum systems where every particle interacts appreciably with every other. Such strongly-interacting many-body quantum systems display some remarkable phenomena that are poorly understood and are impossible to model computationally.

Progress towards these goals relies on the recent great advances in methods for cooling molecules, decelerating and trapping them, and measuring their transition frequencies with unprecedented accuracy. High resolution requires long interaction times, and that requires low temperature. Some species of molecules can now be cooled to milli-kelvin temperatures by laser cooling and, most recently, magneto-optical trapping. Other molecules can be assembled from ultracold atoms, producing micro-kelvin molecules at densities high enough for simulating strongly-interacting quantum systems.

In my talk, I will give a brief overview of these fundamental physics applications and the laser cooling of molecules. Then I will outline our own progress at Imperial College towards two new experiments: a molecular fountain of ultracold YbF molecules for measuring the electron edm, and a lattice of ultracold CaF for quantum simulation.
MOLECULE CHIP: TOWARD HIGH RESOLUTION SPECTROSCOPY (30 min.)

S. BORRI, G. INSERO, P. DE NATALE, G. SANTAMBROGIO.
Istituto Nazionale di Ottica, CNR & European Laboratory for Non-Linear Spectroscopy, LENS, Via Nello Carrara 1, 50019 Sesto Fiorentino, Italy

In the last years, it was demonstrated that neutral molecules can be loaded on a microchip directly from a supersonic beam. Once the molecules are trapped, they can be decelerated to a standstill, for instance, or re-ejected at low speed for high resolution spectroscopic measurements. We control the position of the trapped molecules with an accuracy of a few microns and the molecules are in a single quantum state.

Trapped molecules can be transferred between quantum states with absolute selectivity. This was first demonstrated for rotational transitions, by coupling the molecule chip to a mm-wave radiation source. The technique was then extended into the infrared region using laser light. More recently, we showed time-resolved spatial imaging of molecule on the chip, adding the final fundamental component to the molecule chip. For this, we use resonant-enhanced multi-photon ionization, which is quantum state selective, intrinsically background-free, and of general applicability. Imaging detection allows for the determination of the phase space distribution of the molecules in the microtraps, which we exploited, for instance, for the measurement of the temperature of the trapped molecules.

Now we want to use the molecule chip as a source of cold molecules for high resolution spectroscopy. I will present a miniaturized molecular spectrometer that we are currently developing, which is expected to provide sub-kHz resolution.
OPTICAL PARAMETRIC OSCILLATOR FOR AVANT-GARDE HIGH RESOLUTION SPECTROSCOPY (30 min.)

I. RICCIARDI, CNR-INO, Istituto Nazionale di Ottica, Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy

A highly stable and spectrally pure laser source in the region between 2.7 and 4.2 µm is presented. This laser, based on optical parametric oscillation, combines unique features, such as high power, single mode emission, tunability and wide spectral coverage. In view of demanding applications as frequency metrology, precision tests of fundamental physics, and high-resolution spectroscopy on cold molecular beams, different schemes for the frequency stabilization of mid-infrared idler mode have been implemented. This lecture reviews our latest results about the optical parametric oscillator stabilization.
Poster Session D

Monday, August 24, 16:00
Hydrogen peroxide ($\text{H}_2\text{O}_2$) is one of the molecules being considered as part of the ExoMol project [1] which aims to building a database of line lists for molecules important or the characterization of atmospheres of exoplanets and cool stars. Hydrogen peroxide plays a key role in the chemistry of water and ozone in the planetary atmospheres. Biologically it is important in host defence and in oxidative biosynthetic reactions. Recently, there has been a surge in astrophysical interest in $\text{H}_2\text{O}_2$: It has been detected on the surfaces of Encelades [2] and Europa [3], and as well it is providing insight into surface chemistry in the interstellar medium [4] where it is a possible precursor to the formation of water in the Universe. There is therefore a need for a high-quality, accurate and complete line list for $\text{H}_2\text{O}_2$ as its spectra is highly complex and difficult to characterise. The current HITRAN database contains transitions up to 2000 cm$^{-1}$ which include the torsional and $v_2$ band. However the volatility of hydrogen peroxide makes it a difficult molecule to deal with experimentally, especially at high temperatures. Presented here is a preliminary line list for $\text{H}_2\text{O}_2$ covering the wavenumber range of up to 10 000 cm$^{-1}$ which is compared to currently available experimental data. The synthetic line list was produced using the variational ro-vibrationa l solver TROVE [5] in conjunction with an initial $ab$-$initio$ potential energy surface [6,7] and a new $ab$-$initio$ dipole moment surface. Our goal is a hot line list for this molecule.

References

CAVITY ENHANCED MID-IR/NEAR-IR DOUBLE RESONANCE DETECTION OF ACETYLENE SYMMETRIC STATES

J. KARHU, J. NAUTA, M. VAINIO, M. METSÄLÄ, L. HALONEN, Laboratory of Physical Chemistry, University of Helsinki, Helsinki, Finland

Single photon transitions to symmetric vibrational states of acetylene are forbidden from the ground state. These states have been studied in the past using methods such as laser induced fluorescence\(^1\) and infrared stimulated emission probing\(^2\). We present a novel method for measuring symmetric vibrational states of acetylene, using two consecutive resonant infrared transitions, such as those shown in the energy diagram on the bottom of the page.

The figure below has a schematic picture of the setup. A mid-infrared idler beam from a continuous wave optical parametric oscillator (OPO) traverses the sample cavity once, exciting acetylene molecules to the fundamental \(\nu_3\) stretching vibrational state. Cavity ring down spectroscopy (CRDS) is then used to probe a near-infrared transition to a symmetric vibrational state. The advantages of this method are the high population on the intermediate state, due to the strong fundamental transition and the high power of the OPO idler beam, and the sensitivity of CRDS. The method provides sub-Doppler resolution for the detection of the final rovibrational transition, with a nearly Lorentzian line profile and high signal to noise ratio.


Atmospheric CO$_2$ concentrations are being closely monitored by remote sensing experiments which rely on knowing line intensities with an uncertainty of 0.5% or better. Most available laboratory measurements have uncertainties much larger than this. We report a joint experimental and theoretical study providing rotation-vibration line intensities with the required accuracy. Energy levels were obtained from effective Hamiltonian calculations, while a highly accurate ab initio dipole moment surface (DMS) was calculated at MRCI level. The theoretical model developed above is being used to compute CO$_2$ intensities. Estimation of the theoretical uncertainties involved computation of 4 line lists by cross comparing calculations performed using pairs of potential energy surfaces (PES) and DMS’s. This yields line sensitivities, which are utilized in reliability analyses of our results. The ab initio calculations are extendible to all atmospherically important bands of CO$_2$ and to its isotopologues. Comprehensive line lists for all isotopologues are to be published in the near future.

UNRAVELLING THE CONFORMATIONAL LANDSCAPE OF NICOTINOIDs: THE STRUCTURE OF COTININE IN THE GAS PHASE

I. URIARTE, P. Écija, E. J. Cocinero, Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Apartado 644, 48080 Bilbao (Spain); C. Pérez, CoCoMol, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg (Germany); E. Caballero-Mancebo, A. Lesarri, Departamento Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid (Spain)

Alkaloids such as nicotine, cotinine or anabasine act as nicotinic agonist through binding to the nicotinic acetylcholine receptor, and have been used in the treatment of disorders such as attention/deficit hyperactivity or schizophrenia. These substances share a common floppy structural motif consisting of a two-ring assembly with a 3-pyridil methylamine skeleton. In order to investigate the structure-activity relationship of these biomolecules, structural studies with rotational resolution have been carried out for phenazone, nicotine and anabasine in the gas phase.

We hereby present a structural investigation of cotinine in a jet expansion. First, the rotational spectrum (6-18 GHz) has been investigated thanks to the chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer recently built at the Universidad del País Vasco (UPV-EHU). Two different conformations were detected in the rotational spectrum and both of them display the same “envelope” shape for the five-membered ring. The differences between these two conformations originate from the internal rotation of the two ring moieties, the detected species differing in a near 180° rotation of pyridine. The final structure is modulated by steric effects. Second, the hyperfine structure arising from the presence of two 14N atoms and the internal rotation of the methyl group has been studied thanks to the conventional FTMW spectrometer. The complementarity of both techniques (CP-FTMW and FTMW) has been demonstrated in the structural study of cotinine.

DIRECT COMPARISON OF PDH AND SWEPT LOCKING SCHEMES FOR CAVITY-ENHANCED ABSORPTION SPECTROSCOPY

G. KOWZAN, M. PARADOWSKA, M. BORKOWSKI, P. ABLEWSKI, SZ. WÓJTEWICZ, K. STEC, D. LISAK, R. S. TRAWIŃSKI, P. MASŁOWSKI, Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, ul. Grudziadzka 5, 87-100 Toruń, Poland; K. F. LEE, M. E. FERMANN, IMRA America, Inc., 1044 Woodridge Ave., Ann Arbor, MI, USA 48105

We present an optical frequency comb spectrometer based on Er:fiber laser, operating in the 1.5–1.6 µm range. Comb teeth are locked to a high-finesse cavity (F = 8500). Locking of laser lines is achieved either by a low bandwidth (≈ 20 Hz) swept locking scheme or a two-point Pound-Drever-Hall scheme. Transmission spectrum is resolved by a virtually-imaged phased array etalon and a diffraction grating, which gives a 30 nm-wide spectrum with 1 GHz resolution. Non-linear VIPA dispersion is fitted to measurements of comb line-resolved spectrum of a frequency comb stabilized to a Rb frequency standard, which prevents systematic errors from appearing in frequency axis in the final spectrum.

Using different locking schemes for measurements of the same gas sample allowed us to carefully compare and determine the accuracy and performance limits for various experimental conditions. The PDH locking provides greater sensitivity with lower noise. Since line shape distortions due to dispersion effects can be precisely modeled, this scheme can be applied both in trace gas detection and accurate determination of line shape parameters. The swept scheme avoids the line shape distortions at the price of lower sensitivity. It is based on a commercial lock-in amplifier and low-bandwidth feedback loop.

which makes it a simpler and easier to implement solution, suited for modelocked lasers not equipped with fast actuators.
Chromium Hydride, CrH, is a molecule of both theoretical and experimental interest due to its importance in several astrophysical settings. Under the widely accepted classification of Kirkpatrick, CrH abundance is a key parameter in the identification and characterisation of L-type brown dwarfs; it has also been theoretically proposed by Pavlenko that CrH and CrD could be used to help distinguish brown dwarfs, planets and stars with similar mass and luminosity profiles. It has been speculated that CrH should be found in sunspots and S-type stars. Given CrH’s astrophysical importance and that at present there is no accurate or complete linelist for this molecule, as part of the ExoMol project we aim to bridge this gap.

From a theoretical perspective, CrH is of real interest as, in line with other transition metal hydrides, its spectrum is determined by many, heavily interacting electronic states dissociating to various dissociation limits. Relativistic effects such as spin-orbit coupling are very important as are perturbing states such as the low-lying $^4\Sigma^+$ state.

Here we present a rovibronic line list which can be used for atmospheric modelling up to 2000 K and which has been calculated using the in-house program Duo. To create this line list, potential energy curves, dipole moment curves and couplings between 11 low lying states (up to approximately 20 000 cm$^{-1}$) were calculated using the Multi Reference Configuration Interaction(MRCI) method as implemented in the ab initio quantum chemistry package MOLPRO. Experimentally, the $A ^6\Sigma^+ - X ^6\Sigma^+$ electronic transition of CrH near 861 nm is the only electronic transition of CrH which has been studied; our line list has thus been fitted to the available experimental data. We have made

\begin{itemize}
  \item J.D. Kirkpatrick, Astrophys. J., 519, 802 (1999)
  \item B. Lindgren, G. Olofsson, Astronomy & Astrophysics, 84, 300 (1980)
\end{itemize}
predictions concerning further electronic bands such as $^6\Pi - X^6\Sigma^+$ which should theoretically be observed.
This work was supported by the ERC under Advanced Investigator Project 267219.
It is demonstrated that the use of the $\lambda/2$ method allows one to effectively investigate individual atomic transitions of the $D_2$ line of Cs in strong transverse magnetic fields (with laser radiation of $\pi$-polarization) up to 7 kG. The method is based on strong narrowing of the absorption spectrum (which provides sub-Doppler resolution) of a cesium thin cell with the thickness $L$ equal to a half-wavelength of the laser radiation ($L = \lambda/2$, $\lambda = 852$ nm) resonant with the $D_2$ line. In particular, the $\lambda/2$ method has allowed us to resolve completely 16 atomic transitions which remain in a strong magnetic field (Fig.1). These 16 atomic transitions are contained in two groups of 8 atomic transitions each, and the groups are completely separated for $B > 8$ kG. We have determined their frequency positions, fixed (within each group) frequency slopes, the probability characteristics of the transitions, and other important characteristics of the hyperfine structure of Cs in the hyperfine Paschen-Back (HPB) regime, which means that when a strong magnetic field is applied there is a decoupling of the total angular momentum of electrons $J$ and nuclear momentum $I^{1,2}$. The theoretical model well describes the experiment.

The research was conducted in the scope of the International Associated Laboratory IRMAS (CNRS-France & SCS-Armenia). A. Sargsyan thanks ANSEF Opt 3700 grant for financial support.

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ON DECOUPLING OF TOTAL ELECTRONIC ANGULAR MOMENTUM AND NUCLEAR SPIN FOR $^{39}$K ATOM

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An external magnetic field is required to decouple the total electronic angular momentum $J$ and nuclear spin $I$. Depending on type (as well as isotopes) of atoms different magnetic fields should be used. The threshold for complete decoupling (Hyperfine Paschen Back regime (HPB)) is given by $B \gg B_0 = A_{hfs}/\mu_B$, where $A_{hfs}$ is the ground-state hyperfine coupling coefficient, $\mu_B$ is the Bohr magneton. For $^{39}$K HPB regime starts at $B \gg B_0 = 160$ G, while for $^{85}$Rb $B_0 \sim 0.7$ kG and for $^{87}$Rb $B_0 \sim 2.4$ kG. The study is performed for $^{39}$K $D_1$ line for different resonant light polarizations.

(a) Hyperfine energy levels of $^{39}$K $D_1$ line in a magnetic field ($B < B_0$) and Zeeman transitions for $\pi$-polarization. Selection rules: $\Delta F = 0, \pm 1; \Delta m_F = 0$. Rectangles show GT, dashed lines - two "initially forbidden further allowed" (IFFA) transitions. (b) Atomic transitions in the HPB regime for $\pi$-polarization. Selection rules: $\Delta m_J = 0; \Delta m_I = 0$. Two IFFA transitions are labeled by ovals.

In case of linear polarization and $D_1$ line there are two transitions maintaining their probabilities and frequency slopes. These transitions are so called guiding transitions (GT)\(^1,2\) (Fig. 1 (a)). In HPB regime the transitions come together to GTs, making 2 groups of 4 in each (Fig. 1 (b)). Each transition in the group has the same frequency slope and probability as GT in their group. We use a nano metric potassium thin cell of thickness $\lambda/2$ ($\lambda$ is the resonant light wavelength) allowing us to resolve all individual atomic transitions. The research was conducted in the scope of the International Associated Laboratory IRMAS.

(CNRS-France & SCS-Armenia). A.S. and A.T. thank ANSEF Opt 3700 grant for financial support.
SELECTIVE REFLECTION FROM DENSE Rb\textsubscript{2} MOLECULAR VAPOR

A. PAPOYAN, A. SHMAVONYAN, A. KHANBEKIAN, M. MOVSISYAN, Institute for Physical Research, NAS of Armenia, Ashtarak-2, 0203, Armenia

Selective reflection (SR) of light from an interface of a dielectric window and atomic vapor is a powerful spectroscopic tool for numerous applications\textsuperscript{1}. Using this technique we report the first observation of SR from molecular vapor of Rb\textsubscript{2} dimers formed in all-sapphire sealed-off rubidium vapor cell at the temperature range of 455 – 515\degree C. The SR signals were recorded on various rovibronic components of 1(X)\textsuperscript{1}\Sigma_{g}^{+} – 1(A)\textsuperscript{1}\Sigma_{u}^{+} bound-bound electronic transition of Rb\textsubscript{2} (left graph in Fig.1) by scanning a diode laser frequency in a spectral range of 851 – 854 nm. Mainly SR spectra corresponding to groups of several rovibronic transitions have been recorded.

Left: Relevant Rb\textsubscript{2} potential curves for lower electronic states. Vertical line indicates molecular electronic interstate transition. Right: Rb\textsubscript{2} SR (upper graph) and fluorescence (middle graph) spectra recorded at \( T = 461\degree C \), \( N_{Rb_{2}} = 9.3 \times 10^{15} \text{ cm}^{-3} \); transmission spectra (lower graph) recorded at \( T = 310\degree C \), \( N_{Rb_{2}} = 7.0 \times 10^{15} \text{ cm}^{-3} \) (upper trace) and \( T = 400\degree C \), \( N_{Rb_{2}} = 1.7 \times 10^{15} \text{ cm}^{-3} \) (lower trace). Colored noisy signal superimposed on measured SR spectrum presents the SR spectrum derived from fluorescence by data processing (see text). It is proved that the recorded signals shall be attributed to SR by careful alignment of the measurement setup, as well as by comparison of the experimentally recorded SR spectrum with the modeled one derived from the simultaneously measured fluorescence spectrum using Kramers-Kronig relation and Fresnel formula (right graph in Fig.1). This work was supported by the State Committee of Science MES RA (SCS), in frame of the research project

No.13-1C089. Research partly conducted in the scope of the International Associated Laboratory IRMAS (CNRS-France and SCS-Armenia).
ON-LINE MEASUREMENT OF GASEOUS IODINE DURING A PWR SEVERE ACCIDENT

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Iodine is a highly radio-toxic element, due to its affinity to the thyroid, and represents the major part of the radioactivity released during a nuclear accident. In the context of nuclear safety and radio-protection, we are interested in identifying the iodine gaseous species which are released, in the nuclear power plants, under molecular (I₂) and organic (CH₃I) forms. Therefore, we are working on providing a spectroscopic database for both species. While the infrared spectrum of the ν₆ band of methyl iodide was previously studied¹, only 4000 lines were assigned. We present the rovibrational analysis of a high quality experimental spectrum, of this band, recorded at the AILES beamline of the synchrotron SOLEIL, (780-850 cm⁻¹) with the glowbar internal source. The analysis of this incomplete spectrum was accomplished in collaboration with the LISA and led to 5000 experimental frequencies accurately measured at a resolution of 10⁻³ cm⁻¹. The analysis of the full spectral range is in progress. On the other hand, we tested the C₃v/TDS package of the XTDS² program developed in Dijon on the CH₃I prototype molecule. These results will be shown and discussed. In the case of the molecular iodine, we are developing, in collaboration with the university of Joseph Fourier in Grenoble, an IBB-CEAS (Incoherent Broad Band Cavity Enhanced Absorption Spectroscopy) to measure its absorption spectrum at 520 nm.

This work takes part of the DECA-PF (diagnosis of core degradation by measurement of fission products) project which is supported by the French Na-

tional Agency (ANR) under the PIA program (Programme d’Investissement d’Avenir).
ON THE ”EXPANDED LOCAL MODE” APPROACH APPLIED TO ETHYLENE

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Earlier derived [1-5] for the XY₂ (C₂ᵥ), XY₃ (C₃ᵥ), and XY₄ (T₄) molecules ”expanded local mode model” was applied to the ethylene, X₂Y₄, molecule. On the basis of specially obtained values of the ambiguity parameters, \( \sin \gamma \), simple values of all transformation coefficients, \( l_{N\alpha\lambda} \), were obtained for the C₂H₄ molecule. It gave us possibility

- to derive simple relations between different spectroscopic parameters (harmonic frequencies, anharmonic parameters and rotational-vibrational coefficients) of the C₂H₄ molecule, and

- on the basis of the general isotopic substitution theory [6] to obtain simple values of transformation \( l'_{N\alpha\lambda} \) coefficients for the different isotopic species of the ethylene molecule.

References

HIGH RESOLUTION ANALYSIS OF THE $\nu_4$, $\nu_7$ and $\nu_{12}$ VIBRATIONAL BANDS OF C$_2$D$_4$

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The C$_2$D$_4$ isotopologue is an asymmetric top molecule with twelve different vibrational modes. Because of its symmetry ($D_{2h}$), all the vibrational states of the C$_2$D$_4$ molecule are divided into 8 groups of the states of different symmetry. However, only bands of three types of symmetry are allowed in absorption from the ground vibrational state.

In the present study we consider the $\nu_4$ ($A_u$), $\nu_7$ ($B_u$) and $\nu_{12}$ ($B_u$) fundamental band of the C$_2$D$_4$ molecule which are located in the region of 600 - 1200 cm$^{-1}$. The spectra of these bands were recorded at the Technical University of Braunschweig, Germany, with a Fourier Transform spectrometer Bruker IFS-120 HR at the sample temperature of 300 K, an optical resolution of 0.002 cm$^{-1}$, and pressures of 0.08 and 1.5 mbar using the absorption path length of 4 m.

More than 6000 transitions of the $\nu_4$, $\nu_7$ and $\nu_{12}$ bands were assigned. The ground vibrational state parameters were improved on the basis of analyzed experimental data. As a consequence, about 2000 upper ro-vibrational energies were determined. The Hamiltonian model which takes into account Coriolis resonance interactions between the studied bands was used. Additionally, the influence of the $\nu_{10}$ band, which is absent in our experiment, was taken into account. As the results show, a set of 28 fitted parameters reproduce the initial experimental energy levels with the $d_{rms}=0.0003$ cm$^{-1}$. 
HIGH RESOLUTION SPECTROSCOPIC STUDY OF THE
C$_2$H$_2$D$_2$-cis SPECTRA IN THE REGION OF 580-1210 CM$^{-1}$:
$\nu_4$, $\nu_6$, $\nu_7$, $\nu_8$ and $\nu_{10}$ VIBRATIONAL BANDS

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In the present study we consider the ro-vibrational structure of the $\nu_4$, $\nu_6$, $\nu_7$, $\nu_8$ and $\nu_{10}$ bands of the C$_2$H$_2$D$_2$-cis molecule. C$_2$H$_2$D$_2$-cis is an asymmetric top molecule with twelve different vibrational modes. Because of its symmetry ($C_{2v}$), all vibrational states of the C$_2$H$_2$D$_2$-cis molecule are divided into 4 groups of states of different symmetry.

The FTIR spectra were recorded with a Brucker IFS 120HR Fourier transform infrared spectrometer at Technische Universität Braunschweig. The measurements were carried out in the 580 – 1210 cm$^{-1}$ region at room temperature with sample gas pressures of 0.07 and 1.5 mbar and an absorption path length of 4 m.

For all studied bands transitions have been assigned with higher values of quantum numbers $J_{\text{max}}$ and $K_{a\text{max}}$ than it was made before [1-2]. The assigned transitions were used then in the parameter fit of the effective Hamiltonian. Resonance interactions between all analyzed bands have been taken into account. The set of fitted parameters reproduces experimental line positions with an accuracy being close to experimental uncertainties.

References:

FIRST INVESTIGATION OF THE HERZBERG \((C^{1}\Sigma^{+} \rightarrow A^{1}\Pi)\) SYSTEM IN THE \(^{12}\text{C}^{17}\text{O}\) AND A GLOBAL ISOTOPIC ANALYSIS OF THE \(C^{1}\Sigma^{+}\) RYDBERG STATE

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The \(C \rightarrow A\) (0,1), (0,2) and (0,3) rovibronic bands of the rare \(^{12}\text{C}^{17}\text{O}\) isotope are studied in high resolution using a high-accuracy dispersive optical spectroscopy. Calibration with respect to simultaneously recorded thorium atomic lines, obtained from several overlapped orders of the spectrum in the visible range, as well as a stainless steel hollow-cathode molecular lamp with two anodes, yields an absolute accuracy of wavenumbers measurements of about 0.0025 cm\(^{-1}\) for the CO spectra. All 261 spectra lines of the Herzberg band system in \(^{12}\text{C}^{17}\text{O}\), up to \(J_{\text{max}} = 34\), were precisely measured and rotationally analyzed. As a result, the merged rotational constants and rotational equilibrium constants for the \(C^{1}\Sigma^{+}\) Rydberg state, as well as the band origins, the isotope shifts, the RKR turning points, Franck-Condon factors, relative intensities, and r-centroids of the \(C \rightarrow A\) system in the \(^{12}\text{C}^{17}\text{O}\) isotope were obtained. An experimental RKR potential energy curve and vibrational levels of the \(C^{1}\Sigma^{+}\) state in \(^{12}\text{C}^{17}\text{O}\) together with highly excited \(k^{3}\Pi, c^{3}\Pi, E^{1}\Pi, B^{1}\Sigma^{+}\) and \(D^{1}\Sigma^{+}\) states lying in the region between the first dissociation limit and the ionization potential of CO were plotted. A detailed investigation of possible perturbations that may occur in the \(C^{1}\Sigma^{+}(v = 0)\) Rydberg state of less-abundant \(^{12}\text{C}^{17}\text{O}\) isotope in the close vicinity of the \(k^{3}\Pi(v = 1, 2)\) and \(c^{3}\Pi(v = 0)\) states in the region 92,000 cm\(^{-1}\) was performed. In the \(A^{1}\Pi, v = 3\) state of \(^{12}\text{C}^{17}\text{O}\), extensive, multi-state rotational perturbations were found and analyzed. Also, a global isotopic analysis of the \(C^{1}\Sigma^{+}\) Rydberg state was carried out in the \(^{12}\text{C}^{16}\text{O}, ^{12}\text{C}^{17}\text{O}, ^{13}\text{C}^{16}\text{O}, ^{12}\text{C}^{18}\text{O}, ^{13}\text{C}^{17}\text{O}, \) and \(^{13}\text{C}^{18}\text{O}\) as well as in \(^{14}\text{O}^{16}\text{O}\) and \(^{14}\text{C}^{18}\text{O}\) isotopologues. This analysis enabled us to determine, amongst others, the vibrational equilibrium constants in \(^{12}\text{C}^{17}\text{O}\) for the \(C^{1}\Sigma^{+}\) state, to improve these constants in the \(^{12}\text{C}^{16}\text{O}, ^{13}\text{C}^{16}\text{O}, ^{12}\text{C}^{18}\text{O}, ^{13}\text{C}^{17}\text{O}, \) and \(^{13}\text{C}^{18}\text{O}\) isotopologues and the \(U_{01}\) and \(U_{10}\) isotopically invariant parameters in the CO molecule within the Born-Oppenheimer approximation. It also made it possible to calculate many parameters of the rovibronic structure of the \(C^{1}\Sigma^{+}\) state for eight isotopologues of the carbon monoxide molecule, investigated so far, and to compare them with the theoretical values.
KINETIC AND SPECTROSCOPIC STUDIES OF OZONE USING DOPPLER LIMITED ABSORPTION SPECTROSCOPY AT 28 THz WITH A FREE RUNNING DFB QUANTUM CASCADE LASER

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Quantum Cascade Lasers (QCLs) in the mid-IR range have become now suitable devices for ultra-high resolution laser spectroscopy, molecular trace gas sensors and the study of the possible time dependence of fundamental physical constants.

We present here systematic studies of ozone molecular lines by Doppler absorption spectroscopy over a 1.6 cm$^{-1}$ mode-hop free tuning frequency range of a DFB-QCL centered around 1049 cm$^{-1}$. We apply two different but controllable non-linear corrections on both ramps of the current waveform driving the laser frequency because non-linear spectra are a potential source of systematic bias. The resulting effect is a very efficient linearization of molecular spectra over the full current ramp, leading to a residual error in frequency below $2 \times 10^{-4}$ cm$^{-1}$ over the entire spectrum ($< 2 \times 10^{-7}$).

The laser spectrometer is coupled to two single pass absorption cells, arranged in a parallel setup, which allows for the study of pressure induced line shifts. New pressure shift measurements for individual ozone absorption lines will be presented.

One of the two absorption cells is optimized for kinetic studies and can be heated to temperatures of up to 160$^\circ$C. The rapid scanning of the DFB-QCL permits real time monitoring of the decomposition dynamics of ozone which is investigated at these temperatures using different pressures, bath gases and ozone isotopomers.
SYNCHROTRON-BASED HIGH RESOLUTION STUDY OF THE LOW FREQUENCY VIBRATIONAL MODES OF THREE PANHS: QUINOXALINE, QUINAZOLINE AND INDOLE

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Polycyclic Aromatic Hydrocarbons (PAHs) are astrophysical relevant molecules which are suspected to be present in the interstellar medium since more than thirty years.\(^1\) PAHs and PANHs molecules (PAHs with nitrogen atoms incorporated into the aromatic ring) have been considered to participate of the unidentified infrared emission bands observed in several astrophysical objects. Even if there has been tentative search for specific molecules, there is still no unambiguous detection (based on rotationally resolved spectroscopy) of this molecular family in the ISM.\(^2\)

In the laboratory, these species have mostly been investigated in the microwave domain. For this purpose, PANHs are appropriate species since they possess a larger permanent dipole moment than the purely carbonated PAHs. In the infrared, the data dealing with the analysis of rotationally resolved spectra of PAHs are scarce and limited to cutting edge techniques.\(^3\) At SOLEIL synchrotron facility, the far-infrared radiation extracted by the AILES beamline is optimized in the 50 – 1500 cm\(^{-1}\) spectral range. This emission is modulated by a high resolution interferometer (Bruker IFS 125) and injected in a long absorption pathlength cell (180m).

Recently, this experimental set-up has provided new data about the rovibrational analysis of low frequency vibrational modes of several PANHs in the far-infrared.\(^4\) In this poster, we will present the analysis of four rovibrational modes of three different PANHs occurring in the low frequency part of the far infrared (below 500 cm\(^{-1}\)). \(\nu_{28}\) and \(\nu_{27}\) of quinoxaline centered around 177 and 400 cm\(^{-1}\) respectively, \(\nu_{38}\) of quinazoline around 484 cm\(^{-1}\) and \(\nu_{42}\) of indole centered around 207 cm\(^{-1}\).

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HIGH RESOLUTION SPECTROSCOPY OF SOCl₂ AND ITS ISOTOPOLOGUES: FROM THE MICROWAVE TO THE FAR-INFRARED

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Thionyl chloride (SOCl₂) is a volatile inorganic compound used extensively in industry. Its monitoring in the gas phase is critical for both environmental and defense concerns. The high-resolution gas phase microwave spectrum (below 40 GHz) of the main isotopologue was recorded twenty years ago, however, due to high spectral congestion, no further study of the rotational and rovibrational spectra have been reported. In the present study, the pure rotational and rovibrational spectra of SOCl₂ and its isotopologues have been characterized from the microwave to the far-infrared, using three complementary experimental approaches:

- The chirped-pulse Fourier transform microwave (CP-FTMW) spectrum of SOCl₂ has been recorded in the 7–19 GHz region, revealing pure rotational transitions of rare isotopologues, together with lines of the most abundant ones.

- Pure rotational transitions in the ground and selected vibrationally excited states of SO³⁵Cl₂, SO³⁵Cl³⁷Cl and SO³⁷Cl₂ have been recorded in absorption in the 70–660 GHz region using a frequency multiplication chain.

- For the same isotopologues, the rovibrational spectra of the symmetric $\nu₃$ (344 cm⁻¹) and asymmetric $\nu₆$ (284 cm⁻¹) fundamental bands have been resolved by means of FT-FIR spectroscopy on the AILES beamline of the SOLEIL synchrotron.¹

Fits of all these data have allowed an accurate determination of the molecular parameters (rotational and centrifugal distortion constants, vibrational band centers) and a refined geometry of the molecule has been derived.

SEMICLASSICAL LINE BROADENING CALCULATIONS WITH POTENTIAL ENERGY SURFACE: APPLICATION TO COLLISIONAL EXCITATION OF NH$_3$ BY Ar

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The semi-classical formalism of Robert and Bonamy is used to calculate the half widths of ammonia in collision with argon. Most accurate ab initio potential energy surfaces (PES) of Loreau$^1$ and Bulski$^2$ have been applied to model NH$_3$–Ar interactions.

In this work and contrary to our previous calculations$^3$ we have introduced the transitions $\Delta K = \pm 3n$ into the expressions of the differential collision cross section $S(b)$. Comparison with previous theoretical and experimental studies is performed. A detailed analysis of the contribution of various terms $v_{lm}$ of the PES has shown that the $\Delta K = \pm 3$ transitions play an important role in the calculation.

Calculations made in the $\nu_4$ and $\nu_1$ vibrational bands of NH$_3$ are in good agreement with experimental data and a correct variation of the broadening coefficient with the rotational quantum number J and K is achieved.

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TUNNELING IN MOLECULES PROBED BY HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY

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Removal of an electron from a stable and rigid neutral molecule often results in less stable and semi-rigid singly-charged cations which are subject to large-amplitude motion and quantum-mechanical tunneling. High-resolution photoelectron spectroscopy provides access to the structure and geometry of such cations. Moreover, the distribution of Franck-Condon factors favors the observation of the vibrational modes most strongly affected by the electron removal.

We use pulsed-field ionization zero-kinetic-energy photoelectron spectroscopy to study large-amplitude motion in cations such as butatriene in which photoionization is induced out of double bonds. The photoionization process in these molecules is of particular interest as it introduces torsional flexibility and quantum-mechanical tunneling between equivalent structures along the torsional coordinate.
Among other alkali diatomics the KRb molecule demonstrates a high density of the low-lying electronic states arisen from close energy of the K and Rb atoms in their first excited $^2P$ states. The adiabatic states are mutually perturbed due to the pronounced spin-orbit effect induced by heavy Rb atom and strong configuration interaction. A global deperturbation analysis is apparently required to represent the observed energies and radiative properties of the excited KRb states with the spectroscopic accuracy.

Here we present $R$-depended spin-orbit matrix elements $ab$ initio calculated between all electronic states converging to the lowest four dissociation limits. The relevant quasi-relativistic matrix elements accompanied by the adiabatic potential energy curves were evaluated for a wide range of internuclear distances and density grid in the basis of the spin-averaged wave functions corresponding to pure Hund’s coupling case (a). Both shape and energy consistent small (9-electrons) effective core pseudopotentials were used to monitor a sensitivity of the matrix elements to the particular basis set. The dynamic correlation has been taken accounted by a large scale multi-reference configuration interaction method which was applied for only two valence electrons. The $l$-independent core-polarization potentials of the both atoms were employed to take into account the residual core-valence effect.

The achieved accuracy of the present $ab$ initio functions is discussed by a comparison with preceding calculations$^1$ and their empirical counterparts$^2$ corresponding to the observed spin-orbit splitting between different $\Omega$-components of the triplet $(1)^3\Sigma^+$ and $(1-3)^3\Pi$ states.

All electronic structure calculations were performed with the Molpro package$^3$. The present work was supported by the RFBR under Grant No. 13-03-00466-a.


Recently we studied the rotational spectrum of hydroxyacetonitrile (HOCH$_2$-CN, HAN) in order to provide a firm basis for its possible detection in the interstellar medium$^1$. Different plausible pathways of the formation of HAN in the interstellar conditions were proposed$^2$ however, up to now, the searches for this molecule were unsuccessful. To continue the study of nitriles that represent an astrophysical interest we present in this talk the analysis of the rotational spectrum of 4-hydroxy-2-butynenitrile (HOCH$_2$CC-CN, HBN), the next molecule in the series of hydroxymethyl nitriles. Using the Lille spectrometer the spectrum of HBN was measured in the frequency range 50 – 500 GHz. From the spectroscopic point of view, HBN molecule is rather similar to HAN, because of -OH group tunnelling in gauche conformation. As it was previously observed for HAN, due to this large amplitude motion, the splittings in the rotational spectra of HBN are easily resolved making the spectral analysis more difficult. Additional difficulties arise from the near symmetric top character of HBN ($\kappa = -0.996$), and very dense spectrum because of relatively small values of rotational constants and a number of low-lying excited vibrational states. The analysis carried out in the frame of reduced axis system approach of Pickett$^3$ allows to fit within experimental accuracy all the rotational transitions in the ground vibrational state. Thus, the results of the present study provide a reliable catalog of frequency predictions for HBN. The support of the Action sur Projets de l’INSU PCMI, and ANR-13-BS05-0008-02 IMOLABS is gratefully acknowledged.

AB-INITIO STUDY OF THE I, I’ AND I” $^3\Pi_u$
SUPEREXCITED STATES OF O$_2$

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In this presentation we report progress in the computation of superexcited states of O$_2$, namely, of bound $^3\Pi_u$ Rydberg states of the neutral molecule converging to the $a^4\Pi_u$ state of O$_2^+$. Up to twenty $^3\Pi_u$ potential energy curves were computed. The MRD-CI package together with the cc-pV4Z basis set augmented with seven diffuse functions of s, p and d type on each atom were employed. This study was prompted by the demand of potential curves to try to understand the mechanism of the neutral dissociation of O$_2$ above the first ionization limit (IP= 12.07 eV) where there exists a competition between autoionization and predissociation. This undertaking focuses on the computation of the I, I’ and I” $^3\Pi_u$ states that have been postulated as involved in the neutral dissociation of O$_2$ in the 865-790 Å (14.33-15.69 eV) energy region.
MICROWAVE SPECTROSCOPIC AND QUANTUM CHEMICAL INVESTIGATIONS ON DIMETHYL 1,1-CYCLOPROPANEDICARBOXYLATE

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The structure and dynamics of dimethyl 1,1-cyclopropanedicarboxylate was investigated by a combination of microwave spectroscopy and quantum chemical calculations.

Molecular beam Fourier transform microwave (MB-FTMW) spectroscopy was used as the method of choice for a conformational analysis. Theoretical spectra were obtained by quantum chemistry using the MP2/6-311++G(d,p) level of theory.

Three stable conformers were found by calculating the potential energy surface. Only the most favorable structure with a $C_2$ symmetry was identified in the microwave spectrum and 256 torsional components were assigned. This conformer shows internal rotation due to two equivalent methyl groups. The XIAM program was used for fitting the spectrum with a standard deviation of 2.3 kHz which is close to the experimental accuracy. The rotational constants, centrifugal distortion constants as well as the torsional parameters were determined. The torsional barrier is the same for both methyl groups. Due to the intermediate torsional barrier of $V_3 = 404.59(26)$ cm$^{-1}$, which is in good agreement with the theoretical value, the internal rotation led to splittings of the rotational levels in four components.
NEW SPECTRA OF SO$_2$F$_2$ BELOW 1000 cm$^{-1}$

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Sulfuryl fluoride SO$_2$F$_2$ is an industrial chemical released into the atmosphere in significant quantities$^1$. Therefore it is necessary to model the absorption spectra of this molecule for concentration measurements in the atmosphere and also for theoretical interests as it belongs to quasi-spherical species.

In this work, we present new experimental spectra of the dyad ($\nu_4$, $\nu_5$) in the 380 cm$^{-1}$ region, the bending triad ($\nu_9$, $\nu_7$, $\nu_3$) in the 550 cm$^{-1}$ region and the two bands $\nu_2$ and $\nu_8$ centered at 849.5 and 887.2 cm$^{-1}$ respectively. For these measurements, we used a high-resolution Bruker IFS 125 interferometer with spectral resolution of 0.001 cm$^{-1}$ located at the AILES beam line of the SOLEIL Synchrotron. This equipment was coupled to a multipass cell$^2$ of which the optics were set to obtain a 93 m long absorption path for the dyad and 3 m for the others bands. The SO$_2$F$_2$ sample was cooled to 165 ± 1 K.

We propose afterwards to analyse these bands with a model developed by M. Rotger$^3$ et al. based on the tensorial formalism adapted to XY$_2$Z$_2$ asymmetric tops and C$_{2v}$ symmetry.

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QUANTUM MECHANICAL CALCULATION OF THE MOBILITY OF THE C$^+$ ION IN A COOLED He GAS AT 4.3 K

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On the light of the suggestion mentioned in a recent paper$^1$, we have performed full quantum mechanical calculations of the mobility of C$^+$ ions moving in a cooled buffer helium gas. Hence, this work is realized by the means of the calculated interaction potentials corresponding to ground C$^+$(2P)-He(1S) state and the metastable C$^+$(4P)-He(1S) state which are achieved with MORPLO. Then we use the computed quantum-mechanical transport cross sections in the Viehland gram-char Fortran code as to get the mobility of C$^+$ ions at 4.3 K gas temperature. A good agreement is acquired with the experiment.

MEASUREMENT AND MODELING OF COLD $^{13}$CH$_4$
SPECTRA FROM 2.1 TO 2.7 $\mu$m

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A new study of $^{13}$CH$_4$ line intensities and positions in the Octad region between 3600 and 4800 $\text{cm}^{-1}$ will be reported. Nine spectra were recorded with two Fourier transform spectrometers (the McMath-Pierce FTS at Kitt Peak Observatory and the Bruker 125 HR FTS at the Jet Propulsion Laboratory) using $^{13}$C-enriched samples at temperatures from 299 K to 80 K. Line positions and intensities were retrieved by non-linear least squares curve-fitting procedures and analyzed using the effective Hamiltonian and the effective Dipole moment expressed in terms of irreducible tensor operators adapted to spherical top molecules. Quantum assignments were found for all the 24 sub-vibrational states of the Octad (some as high as J=10). Over 4750 experimental line positions and 3300 line intensities were fitted with RMS standard deviations of 0.004 $\text{cm}^{-1}$ and 6.9 $\%$, respectively. A new linelist of over 9600 measured positions and intensities from 3607 to 4735 $\text{cm}^{-1}$ was produced, with known quantum assignments given for 45 $\%$ of the features.

Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, NASA Langley Research Center, and Connecticut College, under contracts and cooperative agreements with the National Aeronautics and Space Administration. The support of the Groupement de Recherche International SAMIA between CNRS (France) and RFBR (Russia) is acknowledged.
Increasing ring sizes of cycloalkanes are causing increasingly complex conformational properties due to large amplitude vibrations inducing non-planarity. Conformational changes (via ring puckering) of seven-membered rings, such as \(\varepsilon\)-Caprolactone, are prime examples of molecular flexibility with references to chemical implications and possible reaction mechanism for larger molecules containing these motifs. The five lowest lying energy conformers are discussed by their puckering coordinates in a four-dimensional space. To identify the lowest-energy chair and twist-boat conformers of \(\varepsilon\)-Caprolactone supersonic-jet Fourier-transform microwave spectroscopy and high-accuracy quantum chemical investigations are employed. The investigation of the flattened chair structure was conducted by a spectral search of all isotopic species of the ring skeleton in natural abundance. The presence of an ester group in the rectangular flap of the chair warrants an increased staggering and \(\pi\)-electron delocalization, resulting in reduced \(\text{CH}_2\)-bond eclipsing and angle strain. Furthermore, the analysis of the moments of inertia unambiguously identified the second most stable twist-boat species - with the ester group lying approximately in a plane, exhibiting a stabilizing effect.
Precise knowledge of methane absorption is often crucial in the study of planetary systems because its spectral features are used to determine the physical properties of these atmospheres. The Total Internal Partition Sum. 1 2 3 of methane enables one to calculate a wide range of spectroscopic and thermodynamic characteristics. In our approach, we obtain the partition function from 10-3000K by modelling rovibrational energy levels, by consistently combining, for lower polyads individual levels obtained from exact rovibrational calculations and for higher polyads energy levels from statistical estimations based on extrapolations with appropriate physical approximations. In both cases high order contact transformation Hamiltonian was applied 4 to obtain effective Hamiltonian from potential energy surface 5 6. To estimate contributions from higher polyads, we fit the average contributions of the polyads to the partition function obtained from exact calculations at a particular temperature at each polyad with a second order polynomial. The values from the polynomial fit are used to make an estimation formula for higher polyad contributions with the power function to good accuracy. The value of Total internal partition sum is compared with previous reports. This work is supported by French-Russian
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HIGH RESOLUTION OBSERVATIONS OF OH$^+$ AND SH IN TRANSLUCENT INTERSTELLAR CLOUDS

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To date, more than 180 molecules have been identified in the inter- and circumstellar medium. However, only about 10 simple molecules are identified via absorption features originating in translucent interstellar clouds, transparent for optical wavelengths. Spectroscopic characterization of these simple molecules serves as a remote diagnostic of the physical-chemical conditions in such radiation dominated environments, and may help to shed light on the long standing mystery of the diffuse interstellar bands. Here, we present the high resolution near-ultraviolet observations of OH$^+$ and SH in translucent interstellar clouds using the Ultraviolet and Visual Echelle Spectrograph (UVES) of the Very Large Telescope (VLT).

In total, seven rotationally resolved electronic transitions in the OH$^+$ $A^3\Pi$ – $X^3\Sigma^-$ (0, 0) and (1, 0) bands are observed towards CD-32 4348, HD 638 04, HD 78344, and HD 80077. Six of them are identified here for the first time, providing a precise tool to trace OH$^+$ in translucent interstellar clouds. This result is applied to infer the primary cosmic ray ionization rate in the investigated translucent clouds, which yields a typical value of $\sim 1.0 \times 10^{-16}$ s$^{-1}$.\textsuperscript{1}

Sulfur-containing compounds are suggested as important probes of non-thermal processes in the diffuse interstellar medium. From our VLT observational run, we have realized the first detection of rotationally resolved electronic transitions of the mercapto radical (SH) in several translucent interstellar clouds. Two weak absorption features at $\sim$3242.40 and 3240.66 Å, assigned to the $A^2\Sigma^+ – X^2\Pi$ (0, 0) band of SH, are identified, and are found in other published data sets as well. This is the first detection of sulfur-containing molecules in translucent clouds and demonstrates the importance of non-thermal processes, in particular the ion-neutral drift in C-shocks or turbulent dissipation, in the chemical formation of molecules in translucent clouds.\textsuperscript{2}


LINE BROADENING CALCULATIONS FOR METHANE PERTURBED BY DIATOMIC MOLECULES

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We have implemented a semiclassical theory for the calculations of line broadening parameters of infrared lines of methane perturbed by diatomic molecules. In our theory, we include the short range intermolecular interactions, as well as the relevant long range terms (electrostatic). Moreover, the relative trajectories of the molecules are treated classically. Typical calculations involve about 80 radial functions for the potential, as well as several hundreds of Fourier transforms (resonance functions). Our implementation of the theory makes full use of the so-called tetrahedral formalism1. Due to its importance for applications, we first applied the theory to CH₄ perturbed by N₂2. In addition to fundamental and overtone lines, pure rotation lines were also considered3. The theory has subsequently been extended to include other perturbers (H₂ and O₂)4. The calculations need to be improved since, as an example, they do not meet the accuracy requirements of the HITRAN database5. We will show the latest developments of the calculations.

This work was supported by the VAMDC Consortium (Virtual Atomic and Molecular Data Center). We acknowledge financial support from the LEFE-CHAT French National Program. We also thank the GdR SpecMo number 3152 of the CNRS.

ANHARMONIC EFFECTS IN VIBRATIONAL LIGHT-SCATTERING PHENOMENA

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Vibrational light-scattering phenomena are experimentally used to get informations about the structure of molecular systems in spectroscopies as Raman or hyper-Raman spectroscopy. Theoretically, the modeling of these phenomena relies on the computation of high-order molecular properties. In many currently available programs, these properties are computed numerically, meaning an increasing risk of loss of accuracy with the order of the numerical differentiation. Analytic calculation does not entail any such risk.

High-order molecular properties can be calculated analytically at the self-consistent field (SCF) level of theory in atomic orbital basis using an open-ended formulation of response theory\(^1\). A code based on this formulation, OpenRSP, has recently been developed in our team\(^2\). This code currently enables the analytical calculation of molecular properties to arbitrary order, limited by availability of high-order contributions from external routines. Using OpenRSP in conjunction with locally developed external libraries, analytic calculation of a wide range of spectroscopically relevant properties at the Hartree-Fock (HF) and density-functional (DFT) levels is currently possible. Most of the common pure and hybrid functionals are available.

A frequently-used approach when modeling vibrational spectroscopies is the double-harmonic approximation, consisting in treating molecular normal-mode vibrators as harmonic oscillators and modeling spectral intensities using the first geometric derivative of the property governing the spectroscopy of interest. For a more precise treatment of the vibrational frequencies and spectral intensities, anharmonic corrections arising from higher order derivatives should be taken into account as, for example, in the generalized second-order vibrational perturbation theory (GVPT2)\(^3\), where cubic and quartic force fields are required, as well as second and third order geometrical derivatives of the polarization property governing the spectroscopy of interest.

In this contribution, various applications of our approach will be presented. The possibilities offered by our code will be explored through different spec-

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troscopies involving vibrational light-scattering phenomena. Results of anharmonic calculations will be compared to harmonic and experimental ones.
We carried out a calculation of a rovibrational spectrum of the propane (C$_3$H$_8$) molecule with using a hybrid variation-perturbation method [1]. Potential function of the molecule was represented as a quadratic form containing harmonic part and Morse functions for stretching CH bonds. A comparison with the potential function of propane in the database PNNL and experimental spectra form database PNNL showing that we can good to predict frequencies, intensities and rotational structure of the fundamental, overtone and combination absorption bands. This creates the possibility for fast calculations of rovibrational spectra of large hydrocarbon molecules in the overtone absorption region.

The regions of the bending and stretching fundamental bands

The regions of the first overtone and lowest combination bands

This work was supported by the ERC under Advanced Investigator Project 267219.

References
STUDY OF HIGH RESOLUTION RO-VIBRATIONAL SPECTRA OF THE CH$_2$=CD$_2$ MOLECULE: SET OF THE LOWEST FUNDAMENTAL BANDS

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The present study focuses on the high-resolution analysis of the CH$_2$=CD$_2$ molecule in the 600-1310 cm$^{-1}$ region. The absorption spectra of CH$_2$=CD$_2$ were recorded with a Bruker IFS-120 HR FTIR spectrometer at the Technische Universität Braunschweig (Germany) and Nanyang Technological University (Singapore), under different experimental conditions. There are six fundamental bands in the studied region: $v_{10}$ ($B_1$), $v_7$ ($B_2$), $v_4$ ($A_2$), $v_8$ ($B_2$), $v_3$ ($A_1$) and $v_6$ ($B_1$).

For the description of the upper ro-vibrational levels, the effective Hamiltonian model which takes into account resonance interactions between all six vibrational states was used. More than 10 000 transitions were assigned with maximum values of upper quantum numbers $J_{\text{max}}=44$ and $K_{\text{a max}}=19$. As the result, a set of obtained parameters reproduces the initial experimental data with an accuracy close to experimental uncertainties.
Invited Lectures E,
Mini-Symposium, Spectroscopy of planetary atmospheres
Tuesday, August 25, 9:00
Chair : A. PERRIN
SPECTROSCOPIC SIGNATURE OF ORGANIC MOLECULES IN TITAN’S ATMOSPHERE (30 min.)

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The Composite Infrared Spectrometer (CIRS) on-board Cassini has recorded spectra of Titan’s atmosphere in the far and mid-infrared since 2004 with a spectral resolution of up to 0.5 cm\(^{-1}\). Mismatch between observed spectra and model spectra obtained from the available line lists has led us to study the spectroscopic parameters of HC\(_3\)N [1], C\(_4\)H\(_2\) [2] and C\(_2\)N\(_2\) [3], the longest gas phase carbon chains observed so far on Titan. Band intensities, hot band intensities, and line lists were systematically verified by comparison with new laboratory spectra. Erroneous band intensities as well as an absence or shortage of hot band transitions in the line lists leading to model-data mismatches and inaccurate quantifications have been found. We have recently published revised band intensities for the bending modes of C\(_4\)H\(_2\) that could lead to significant change to the quantification of this molecule [4]. Improvement in the spectroscopic parameters has led to the detection in Titan’s atmosphere of \(^{13}\)C isotopologues of HC\(_3\)N [5] and C\(_4\)H\(_2\) [2]. The study on C\(_2\)N\(_2\) opens the way to the detection of \(^{15}\)N isotopologues whose abundances could give some clues to understand the origin and the evolution of Titan’s atmosphere. Also, the higher accuracy of spectroscopic data used to model CIRS spectra facilitates the search for longer carbon chains on Titan such as HC\(_5\)N, C\(_6\)H\(_2\) and C\(_4\)N\(_2\). Our recent measurements obtained at the SOLEIL synchrotron far infrared beam line of band intensities of C\(_4\)N\(_2\) in the far and mid infrared domain have shown strong discrepancies with previous results. Following the intensity measurements, a careful analysis of high resolution data has led to the first line lists for C\(_4\)N\(_2\), which has given us the chance to determine a precise abundance upper limit for this molecule in Titan’s atmosphere [6].


ACCURATE REMOTE SENSING OF GREENHOUSE GASES IN THE EARTH’S ATMOSPHERE (30 min.)

ANDRÉ BUTZ. Karlsruhe Institute of Technology (KIT), IMK-ASF, Leopoldshafen, Germany

Man-made emissions of the greenhouse gases carbon dioxide and methane largely drive current changes in the climate system. Therefore, quantifying the sources and sinks of these gases is key to understanding and projecting climate change and to potentially develop efficient mitigation measures. Sources and sinks at the ocean and land boundaries can be estimated by relating spatiotemporal variations of the atmospheric concentration fields to emission or uptake processes at the Earth’s surface. Accurate remote sensing of carbon dioxide and methane from satellite platforms has become feasible through satellites such as the Greenhouse Gases Observing Satellite (GOSAT) and the Orbiting Carbon Observatory (OCO-2). Their global coverage and relatively high data density promises new insight into the relevant surface processes. The most promising observation technique relies on measuring molecular absorption bands in shortwave-infrared (SWIR) sunlight backscattered by the Earth’s surface and atmosphere. However, the required accuracy on the order of fractions of a percent is unprecedented for planetary remote sensing of atmospheric composition. Therefore, dedicated radiative transfer models and retrieval schemes need to be developed. Spectroscopic parameters and line shape models driving the radiative transfer calculations need to comply with the subpercent accuracy goal in order to avoid biases depending on observation geometry. Ground-based remote sensing tools need to be established to calibrate and validate the satellite soundings. Here, I report on methods and tools developed for spectroscopic remote sensing of carbon dioxide and methane from space and ground and I will highlight some results on the current state of the carbon and methane cycles.
NATURAL AND ANTHROPOGENIC CONTRIBUTIONS TO THE ATMOSPHERIC COMPOSITION VARIABILITY AS OBSERVED FROM SPACE (30 min.)

G. DUFOUR, M. EREMEMKO, J. CUESTA, G. FORET, M. BEEKMANN, A. CHEINEY, J.-M. FLAUD, Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR 7583, CNRS, UPEC, UPD, Créteil, France; C. DOCHE, Météo France, Direction Inter-Régionale Sud-Ouest, Division Études et Climatologie, Mérignac, France; Y. WANG, Z. CAI, Y. LUI, Key Laboratory of middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China; M. TAKIGAWA, Y. KANAYA, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan

Air quality monitoring from space gives a helpful complement to in situ measurements and regional chemical transport models (rCTM) in order to draw a more comprehensive picture of pollution processes. Important progresses in the field of atmospheric sounding from space have been accomplished during the last decade. Lower tropospheric ozone is now available from IASI (Infrared Atmospheric Sounding Interferometer) with a maximum of sensitivity between 3 and 4 km. The availability of semi-independent columns of ozone from the surface up to 12 km simultaneously with CO columns from IASI provide a powerful observational dataset to identify the natural and anthropogenic processes controlling tropospheric ozone enhancement at synoptic scales. We use satellite observations from IASI on board the MetOp satellite to determine the respective role of natural (transport) and anthropogenic (pollution) in the day-to-day variability of lower tropospheric ozone over East Asia. We show that the succession of low- and high-pressure systems largely influence this variability. A case study analysis in May 2008 shows that reversible subsiding and ascending ozone transfers in the UTLS region occurring in the vicinity of low-pressure systems and associated with tropopause perturbations affect the free and lower tropospheric ozone over large regions north to 40°N and largely explain the ozone enhancement observed with IASI in the North Asian troposphere. Over Chinese highly polluted regions, the analysis of ozone observations in correlation with CO and NO2 observations reveals a more complex situation where the photochemical production of ozone often plays a concomitant role to explain ozone enhancements in the lower troposphere.
Poster Session F

Tuesday, August 25, 11:00
Methanol is an asymmetric near-prolate top molecule exhibiting a low frequency internal torsional vibration around the C-O bond. High resolution spectroscopic experiments on methanol were carried out mainly in the fundamental range and low-energy combination bands. But the overtone range is almost unexplored at high resolution due to its complexity and small absorption cross sections. Only low resolution studies have been published yet.

In this work, we present the first high resolution OH-stretch overtone experimental spectra. A direct absorption tunable diode laser spectrometer was used to record spectra between 7180 – 7220 cm$^{-1}$ at three low temperature (13, 23, and 56 K) in planar jet supersonic expansion. Despite the significant rotational cooling at those jet temperatures the spectrum is still very complex due to high density of rovibrational states including the methanol internal torsion. To overcome this complexity, the combination of two temperature analysis (TTA) with ground state combination differences (GS CDs) method were used to determine assignments at least for some of the lowest rotational states.

In the presented analysis, spectra measured at 13 and 56 K were used to perform the TTA which provided a restricted set of possible assignments for each line. Next this information has been used in combination with the GS CDs method to provide reliable spectral assignments for transitions from the lowest

rotational levels. Multiple transitions are observed with the same rotational assignments indicating presence of another NIR-active vibrational state in this spectral range.
Amat Mills Award Applicant

FIRST HIGH-RESOLUTION OVERTONE DATA FOR TRANS-FORMIC ACID IN THE SUPersonic JET

V. SVOBODA, J. RAKOVSKÝ, V. HORKÁ-ZELENKOVÁ, P. PRACNA, and O. VOTAVA, J. Heyrovský Institute of Physical Chemistry of the ASCR, v. v. i., Dolejškova 2155/3, 182 23 Prague 8, Czech Republic

Formic acid is a basic carboxylic acid and one of the simplest molecules exhibiting rotational isomerism1 (cis- and trans-). Its long-lasting spectroscopic interest originates also from the fact that it has been observed in interstellar clouds and in upper troposphere of the Earth2. However, only few papers3,4,5 present high-resolution overtone data. It is probably due to problems raised by the density of the rotational structure for the vibrational bands in a molecule of this size.

In this work, the first high-resolution measurement of OH-stretch overtone of trans-formic acid in the jet at 37 K has been made. The data fully cover region between 6950 and 6995 cm\(^{-1}\) where roughly 600 lines from the lowest rotational states have been identified. To perform line assignments, a new program for assignment using ground state combination differences (GSCDs) method has been developed. Using the program, 246 lines have been reliably assigned and consequently energies for more than 40 upper ro-vibrational levels of the OH-stretch overtone vibration have been experimentally determined. A fit using ro-vibrational Watson’s type Hamiltonian has been performed using PGOPHER program. Some perturbed upper levels have been identified for

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the first time. In addition, some levels not belonging to OH-stretch overtone have been recognised. Their inclusion into the fit will require a subsequent work.
Protonated molecules such as $\text{H}_3^+$, $\text{N}_2\text{H}^+$, $\text{HCO}^+$ are transient species relatively abundant in the interstellar medium. In particular $\text{H}_3^+$ is involved in several physico-chemical processes of the interstellar medium. Protonated rare gases are also considered as relevant species for astrophysics. This has been illustrated by the recent detection of $^{36}\text{ArH}^+$ using the Herschel satellite. In contrast, the detection of $\text{HeH}^+$ (of high importance for the early universe chemistry) is still lacking.

In the laboratory, such species can be produced in a hollow cathode discharge cell and most of the data from the literature have been obtained from tunable far-infrared techniques (to record the pure rotation transitions in the ground state) as well as from laser-based techniques (to study the rovibrational excited states). On the AILES beamline of SOLEIL synchrotron facility, we have developed a liquid nitrogen cooled hollow cathode discharge cell to record absorption spectra of such molecules. This new experimental device, coupled with the AILES beamline Fourier transform spectrometer is a powerful tool to record broadband high resolution spectra of molecular ions in the far-infrared.

This technique appears to be very complementary to tunable far-infrared laser techniques possessing a higher sensitivity but covering a narrower spectral range.

In this poster, we will show experimental results and analysis of three protonated rare gases ($\text{ArH}^+$, $\text{KrH}^+$ and $\text{XeH}^+$, including several isotopic species) that we have obtained in the far-infrared (pure rotation) and in the mid-infrared regions (rotation-vibration). We will also expose preliminary results that we have obtained by modulated the concentration of $\text{N}_2\text{H}^+$ in the plasma. This technique based on the concentration modulation technique used in laser spectroscopy has been adapted to the fast scan spectrometer of the beamline in order to increase the signal to noise ratio of our spectra and get some insights in the chemical dynamics occurring in the discharge.

\[ \text{1. T. Oka, PNAS, 103, 12235 (2006). doi:10.1073/pnas.0601242103} \]
Knowledge of rovibrational transitions of hydrocarbons (C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{4}) is of primary importance in many fields but remains a formidable challenge for the theory and spectral analysis. Essentially two theoretical approaches for the computation and prediction of spectra exist. The first one is based on empirically-fitted effective spectroscopic models. Several databases aim at collecting the corresponding data but the information about C\textsubscript{2}H\textsubscript{4} spectrum present in these databases remains limited, only some spectral ranges around 1000, 3000 and 6000 cm\textsuperscript{-1} being available. Another way for computing energies, line positions and intensities is based on global variational calculations using \textit{ab initio} surfaces. Although they do not yet reach the spectroscopic accuracy, they could provide reliable predictions which could be quantitatively accurate with respect to the precision of available observations and as complete as possible. All this thus requires extensive first-principles quantum mechanical calculations essentially based on two necessary ingredients: (i) accurate intramolecular potential energy surface and dipole moment surface components and (ii) efficient computational methods to achieve a good numerical convergence. We report predictions of vibrational and rovibrational energy levels of C\textsubscript{2}H\textsubscript{4} using our new ground state potential energy surface obtained from extended \textit{ab initio} calculations\textsuperscript{1}. Additionally we introduce line positions and line intensities predictions based on a new dipole moment surface for ethylene. These results are compared with previous works on ethylene and its isotopologues.

This work is supported by French-Russian LIA SAMIA and Tomsk State University Mendeleev grant program.

\textsuperscript{1}T. Delahaye, A. V. Nikitin, M. Rey, P. G. Szalay, and Vl. G. Tyuterev, J. Chem. Phys. 2014, 141, 104301
As has been previously shown, the in-phase/quadrature phase modulation passage-acquired coherence technique (IMPACT) Fourier-transform microwave (FT-MW) spectrometer delivers broadband capabilities at highest spectral resolution. Nevertheless due to specific details in the electronic setup the applicable maximum polarization power was limited. Hence less polar molecules were difficult to measure.

In a novel approach this disadvantage could be circumvented by use of the polarization direction of the microwave radiation. The setup prevails the high spectral resolution but increases the sensitivity dramatically while allowing the utilisation of very high power tube amplifiers.

In this contribution we present the novel apparatus in detail and first experimental results obtained with the modified spectrometer.
Our ability to smell depends on interactions between molecules that are chiral – they exist as enantiomers, mirror images that are not superposable on each other. There are enantiomers that smell differently while others have the same odour. These different responses to enantiomers are puzzling and refer to a most fundamental question that is still unsolved: how does the human olfactory system recognize an odorant? What are the molecular mechanisms by which odorants are identified? Enantiomers constitute interesting models to explore the factors that determine receptor response. It has been proposed that enantiomeric discrimination is related to molecular flexibility. To test this hypothesis, we are investigating the conformational space of several odorants with enantiomers that produce different responses from olfactory receptors using a chirped-pulse Fourier transform microwave spectrometer recently built at King’s College London. Here we present first results on the conformers and structures of several odorants.
SMALL MOLECULES IN EXTERNAL MAGNETIC FIELDS

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In this work we study properties of the molecular ions H$_3^+$ and H$_2^+$ in the electronic ground states when placed in a uniform weak magnetic field. Two methods were considered for the calculation of the electronic energy: perturbation theory and a fully variational approach by means of trial functions which contain magnetic terms. Results were obtained within the Born-Oppenheimer approximation. For H$_3^+$, potential energy surfaces (PES) were calculated using standard ab initio methods. The magnetic interaction terms were then evaluated by first order perturbation theory for fields of up to 2350 T (0.01 $B_0$ in atomic units). These terms were fitted to a functional form and the deformations of the field-free PES investigated. For H$_2^+$, potential energy curves were obtained variationally using tailored trial functions, $0 \leq B \leq 2.35 \times 10^5$T (1.0 $B_0$), for different orientations. Ro-vibrational energy levels were computed considering the full nuclear Hamiltonian. Below, the rotational structure of the four lowest vibrational states is shown for $B = 0.2 B_0$.

VIBRATIONAL STATES OF THE TRIPLET ELECTRONIC STATE OF H$_3^+$: THE ROLE OF NON-ADIABATIC JAHN-TELLER COUPLING

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Vibrational energies and wave functions of the triplet state of the H$_3^+$ ion have been determined$^1$. In the calculations, the ground and first excited triplet electronic states are included as well as the most important part of the non-Born-Oppenheimer coupling between them. The diabatization procedure proposed by Longuet-Higgins is then applied to transform the two adiabatic potential energy surfaces of the triplet-H$_3^+$ state into a $2 \times 2$ diabatic matrix. The diabatization takes into account the effect of the geometrical phase due to the conical intersection between the two adiabatic potential surfaces. The results are compared to the calculation involving only the lowest adiabatic potential energy surface of and neglecting the geometrical phase. The energy difference between the two sets of calculations is about one wave number for the lowest vibrational levels. The figure shows contour plots of the two adiabatic components of the lowest vibrational state for three values of the hyperradius, $R$. Due to the conical intersection a geometrical phase of $\pi$ is built up in the circular coordinate, clearly seen as discontinuity in the 6 o’clock position.

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Non-adiabatic corrections to ro-vibrational levels of small molecules are necessary to account for the experimental accuracy of few cm\(^{-1}\). However, general ab initio calculations of these corrections are at present out of reach. In a recent work\(^1\), we introduce the separation of motions of the nuclei plus a fraction of electrons that they pull in their movement (the core) and the fraction of immobile electrons (the valence). These fractions depend on the nuclear distances \(R\). In consequence, a nuclear equation is obtained in which the nuclear reduced mass is replaced with the \(R\)-dependent core reduced mass \(\mu(R)\). Except for the effects of avoided-crossings (or intersections), this approach accounts very well for the non-adiabatic effects. The ro-vibrational levels are usually calculated with very accurate PECs (PESs) augmented with DBOC (diagonal Born-Oppenheimer corrections) and relativistic corrections. The non-adiabatic corrections to the ro-vibrational levels are obtained as the difference between the energies of these states calculated with \(\mu(R)\) and those calculated with the reduced mass of the bare nuclei. \(\mu(R)\) is obtained from the molecular electronic structure of the molecule. Two recipes have been developed in our group so far. For H\(_2^+\), H\(_2\) and their isotopologues\(^2\) and H\(_3^+\)\(^3\), the diagonal Mulliken populations are taken as the core electron fractions attached to the nuclei. Results are quite good and the first mass surface was developed for H\(_3^+\). For LiH, Mulliken populations do not describe the electronic density appropriately for our purposes. A combination of valence bond ionic and covalent components gives the best results so far\(^4\).

The VBCI orbitals show to be quasi-orthogonal, allowing an interpretation of the bonding in LiH as resulting from a quantum superposition of one-electron ionic and covalent states.
FITS USING A NEW HYBRID PROGRAM OF THE MW SPECTRA OF 2-METHYLMALONALDEHYDE AND AMMONIA-WATER COMPLEX

ISABELLE KLEINER, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 (CNRS/Universités Paris Est & Paris Diderot), 61 avenue du Général de Gaulle, F-94010 Créteil cedex, France; JON T. HOUGEN, Sensor Science Division, NIST, Gaithersburg, MD 20899-8441, USA

A hybrid Hamiltonian formalism using a 2×2 partitioned Hamiltonian matrix for molecules with one internal C3v rotor (which is treated in the 1,1 and 2,2 blocks by traditional expressions for the kinetic energy operator and three-fold potential energy function, and its higher-order torsion-rotation correction terms) and one back-and-forth motion (which is treated by a tunneling formalism in the 1,2 and 2,1 blocks) has been written and reported on in earlier meetings (BOLOGNA2014 and ISMS2015). We present here nearly final fits using this hybrid program of over 2500 microwave transitions for both 2-methylmalonaldehyde-d0 and -d1 (where deuteriation is in the OH group of O=CH-C(CH3)=CHOH). (In 2-methylmalonaldehyde, the methyl group is the internal rotor, and hydrogen transfer from the -O-H group to the O=C-group is the back-and-forth motion.) The new fits with the hybrid program resolve a puzzle in an earlier treatment of these data using a pure tunneling formalism1, since the new fits give values of V3(OH) = 304 cm\(^{-1}\) ≈ V3(OD) = 316 cm\(^{-1}\), which bring the barrier heights for these two isotopologues into much closer agreement. We also present some preliminary fits using the new hybrid program of microwave and far-infrared transitions of the H3N–HOH complex which show promise for improving the fitting situation presently in the literature2. (In the ammonia-water complex, ammonia is the internal rotor, and exchange of the water hydrogens in the N–H hydrogen bond is the back-and-forth motion.)

STRONG THERMAL NONEQUILIBRIUM IN HYPERSONIC CO AND CH₄ PROBED BY CRDS

M. LOUVIOTᵃ, N. SUAS-DAVIDᵇ, V. BOUDONᵃ, R. GEORGESᵇ, M. REYᶜ, S. KASSIᵈᵃ Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS–Univ. Bourgogne Franche-Comté, 9 Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France,ᵇ Institut de Physique de Rennes, UMR 6251, Campus de Beaulieu, Bât 11C, Université de Rennes 1/CNRS, F-35042 Rennes Cedex, France,ᶜ Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, UFR Sciences Exactes et Naturelles, BP 1039, F-51687 Reims Cedex 2, France,ᵈ Laboratoire Interdisciplinaire de Physique, Université Grenoble 1/CNRS, LIPhy UMR 5588, Grenoble F-38041, France

A new experimental set-up coupling a High Enthalpy Source (HES) reaching 2000 K to a cw Cavity Ring-Down Spectrometer has been developed to investigate rotationally cold hot bands of polyatomic molecules in the [1.5, 1.7] µm region. The rotational and vibrational molecular degrees of freedom are strongly decoupled in the hypersonic expansion produced by the HES and probed by Cavity Ring-Down Spectroscopy. Carbon monoxide has been used as a first test molecule to validate the experimental approach. Its expansion in argon led to rotational and vibrational temperatures of 6.7 ± 0.8 K and 2006 ± 476 K, respectively. The Tetradecad polyad of methane (1.43 µm) was investigated under similar conditions leading to rotational and vibrational temperatures of 13 ± 5 K and 750 ± 100 K, respectively. The rotationally cold structure of the spectra reveals many hot bands involving highly excited vibrational states of methane¹.

Schematic drawing of the experimental setup.

INFRARED SPECTROSCOPY OF RUTHENIUM TETROXIDE
AND HIGH-RESOLUTION ANALYSIS OF THE $\nu_3$ BAND

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After the Fukushima accident, it became essential to have a way to monitor
in real time the evolution of a nuclear reactor during a severe accident, in
order to react efficiently and minimize the industrial, ecological and health
consequences of the accident. Through the French program ANR ”projet
d’investissement d’avenir”, the aim of the DECA-PF project (diagnosis of
core degradation from fission products measurements) is to monitor in real
time the release of the major fission products (krypton, xenon, gaseous forms
of iodine and ruthenium, aerosols) outside the nuclear reactor containment.

These products are released at different time during a nuclear accident and at
different states of the nuclear core degradation. Thus, monitoring these fission
products gives information on the situation inside the containment and helps
to apply the Severe Accident Management procedures. Ru is a fission product
of uranium and can be created, under its volatile form RuO$_4$, after an air inlet
in the reactor vessel. RuO$_4$ is a high radiotoxic fission product (isotopes 103
and 106 of ruthenium). The presence of RuO$_4$ is also a marker of the vessel
rupture by molten corium. For these reasons, the possible remote sensing of
this compound in the atmosphere has gained technological importance and
motivated this study. In this poster, we present new experimental results,
using Synchrotron Radiation (French synchrotron facility SOLEIL on the in-
frared beam line AILES) coupled to a high resolution FTIR spectrometer and
new gas handling facilities to study the vibrational spectra of RuO$_4$. New,
higher resolution ($0.001$ cm$^{-1}$) spectra of the $\nu_3$ region of natural abundance
RuO$_4$ and pure $^{102}$RuO$_4$ have been recorded. Using the tensorial formalism
and methods developed at Dijon (ICB), spectra are analyzed in detail for the
five main isotopologues by considering $\nu_3$ as an isolated band. We can also
give a precise value for the isotopic shift of the $\nu_3$ band and the spectroscopic
parameters of the two minor stable as well as the two radioactive isotopologues.
can be estimated\textsuperscript{1}.

DUO: A GENERAL MULTI-STATE PROGRAM FOR SOLVING THE NUCLEAR MOTION SCHRÖDINGER EQUATION FOR DIATOMIC MOLECULES WITH ARBITRARY COUPLINGS

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Although solution of the diatomic nuclear motion problem for a single, uncoupled potential energy curve is standard, there appears to be no general rovibronic program available for diatomics characterized by complex interactions between electronic states. We have therefore developed a new computational tool, DUO, to fill this gap. DUO is a flexible, user-friendly program written in Fortran 2003 capable of solving the Schrödinger equation for the nuclear motion of a general diatomic molecule with an arbitrary number and type of coupling between electronic states. The program is based on a unique computational approach allowing one to build diatomic ‘projects’ from a set of pre-defined objects such as potential energy and dipole moment functions, spin-orbit, electronic angular momentum, spin-rotational, Λ-doubling terms etc. From these objects DUO computes energy levels, line positions and line intensities. Several analytic forms plus interpolation and extrapolation options are available for representation of the curves. DUO can refine potential energy and coupling curves to best reproduce reference data such as experimental energy levels or line positions.

Duo is currently being used as a diatomic computational tool as part of the ExoMol project, whose aim is to generate high-temperature spectra for all molecules likely to be observable in exoplanet atmospheres in the foreseeable future. Examples of Duo calculations for ExoMol molecules include AlO, ScH, CaO, VO, PO and PS.

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MODELLING HIGH-RESOLUTION ABSORPTION SPECTRA WITH EXOMOL LINE LISTS: NH3 AND CH4

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The conditions, chemical reactions and gas mixing in industrial progresses as for example gasification or combustion can be monitored by in situ measurement of gas temperature and gas composition. This can be done spectroscopically, though the result is highly dependent on the quality of reference data [1]. For this reason, a collaboration has been established between the Optical Diagnostics Group at Danish Technical University (DTU) and the ExoMol group at University College London (UCL), to combine high resolution spectra measured at elevated temperatures and empirically tuned ab initio methods to produce suitable molecular line lists for modelling NH3/CH4 in combustion or gasification processes.

The current focus is on industrially important molecules NH3 and CH4 for which high temperature line lists, BYTe [2] and YT10to10 [3], are already available from ExoMol. These line lists were used by Canty et al. (2015) [4] to assign methane and ammonia features in the spectra of late-T dwarfs. High-resolution absorption spectra (0.01 cm$^{-1}$) of NH3 in the region 500 - 2100 cm$^{-1}$ at temperatures up to 1027°C and about atmospheric pressure are measured. The high temperature spectra are analysed by comparison to BYTe and experimental energy levels determined using the MARVEL procedure. Approximately 2100 lines have been assigned, of which 972 are newly assigned to mainly hot bands from vibrational states as high as $v_2 = 5$ [5]. A summary of our results will be presented. Also presented will be a comparison of high-resolution absorption spectra of CH4 at 500°C with YT10to10.

TEMPERATURE DEPENDENCE OF CO₂-COLLISIONAL BROADENING OF ACETYLENE LINES

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Acetylene is a minor constituent of the Earth’s atmosphere¹ and is also present on Mars², Titan³ and Jupiter⁴. Previous studies of the collisional broadening coefficient of C₂H₂ lines have been mainly performed for perturbers like N₂⁵, O₂⁶, H₂ and nobel gases⁷. Few studies have been devoted to the CO₂-broadening coefficient of acetylene⁸. However, this spectroscopic parameter is very useful to study atmospheres where carbon dioxide is widely present like Mars or Venus.

In this present work, we have measured CO₂-collisional broadening coefficients of absorption lines in the ν₄ + ν₅ band of C₂H₂ at low temperature. For each line and temperature, spectra have been recorded for 4 different pressures of CO₂. The experimental lineshape have been individually fitted with the Voigt and the Rautian-Sobel’m and Galatry models, which include the collisional narrowing (Dicke effect). From these fits, we have deduced the collisional half-widths at each pressure and determined precisely the CO₂-broadening coefficients at each temperature. In this method, the self-broadening contribution of C₂H₂ to the total half-width have been taken into account. Finally, we have deduced the temperature dependence of the CO₂-broadening coefficient from our results obtained at different temperatures.

N$_2$-COLLISIONAL BROADENING OF METHANE LINES AT LOW AND HIGH TEMPERATURES

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Methane is an abundant organic trace gas which plays an important role on climate and chemistry in the Earth’s atmosphere$^1$. This important greenhouse gas is naturally present on Earth but mainly due to the human activities$^{2,3}$. The interest in CH$_4$ remains also in the fact that it has been detected in others planets$^{4,5}$ and stellar objects$^6$. In order to have accurate retrievals, it is needed to determine, with a good precision, the spectral parameters$^7$ like the collisional broadening coefficient and its temperature dependence.

To study the N$_2$-broadening coefficient of absorption lines in the $\nu_3$ band of methane, we have used an improved tunable diode-laser spectrometer. The setup has been coupled with low and high temperature cells in order to determine the temperature dependence.

For each line and temperature, we have recorded spectra at four pressures of nitrogen. For each spectrum, the experimental lineshape has been fitted with the Voigt profile and the Rautian and Galatry models, who take into account the collisional narrowing (Dicke effect). The collisional broadening coefficient is given by the slope of the best straight line through the experimental data in a collisional half-width versus the nitrogen pressure representation. The temperature dependence parameter has been deduced from these results for the three considerate profiles. Finally, the results are compared with previous studies available in the literature.

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PRESSURE BROADENING AND SHIFTING COEFFICIENTS AS TESTS OF H$_2$(D$_2$)-He POTENTIAL ENERGY SURFACES

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We have calculated the helium-pressure broadening and shifting coefficients of the isotropic Raman Q(1) lines of the fundamental of H$_2$ and D$_2$. The quantum dynamical close coupling calculations were performed on five 3-dimensional PESs, namely: the pot3d potential of Bakr et al.\(^1\) the so-called BMP PES\(^2\) the modified Muchnik and Russek PES\(^3\) the modified BMP PES\(^1\) and the Schaefer and Köhler PES\(^4\). The last one being the oldest one and obtained at the lowest-level of quantum chemical accuracy but has the advantage of covering interactions over a larger intramolecular interval. Moreover, the theoretical values it leads to\(^5\) are in quite good agreement with experimental pressure broadening and shifting coefficients\(^7\).\(^6\)\(^7\)\(^8\)\(^9\)\(^10\) By decomposing the kinetic energy dependent pressure broadening cross-sections in an inelastic part and a dephasing one and by also looking at the isotropic contribution of the pressure shifting cross-sections allow us to bring to the fore the main differences that exist between the five PESs we have considered. The modBMP PES has been readily rejected because it is only a slight modification of the original BMP PES. The BMP and modMR PESs lead to thermally averaged values far from the experimental ones. The quantum chemical ”state of the art” PES of Bakr et al provides shifting parameters in better agreement than the SK PES with experimental shifts but, the broadening parameters seem to be slightly more accurate with the SK PES. This last point should be confirmed by an accu-

rate lineshape analysis taking into account possible sources of inhomogeneous broadening.
MILLIMETER-WAVE MEASUREMENTS AND AB INITIO CALCULATIONS OF THE NH$_3$–CO COMPLEX

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The rotational spectrum of the van der Waals complex NH$_3$–CO has been measured with the intracavity OROTRON jet spectrometer in the frequency range of 112-139 GHz. Newly observed and assigned transitions belong to the $K = 0 - 0$, $K = 1 - 1$, $K = 1 - 0$ and $K = 2 - 1$ subbands correlating with the rotationless $(j_k)_{NH_3} = 0_0$ ground state of free ortho-NH$_3$ and the $K = 0 - 1$ and $K = 2 - 1$ subbands correlating with the $(j_k)_{NH_3} = 1_1$ ground state of free para-NH$_3$. The (approximate) quantum number $K$ is the projection of the total angular momentum $J$ on the intermolecular axis. Some of these transitions are continuations to higher $J$ values of transition series observed previously$^1$, the other transitions constitute newly detected subbands. The new data were analyzed together with the known millimeter-wave and microwave transitions in order to determine the molecular parameters of the ortho-NH$_3$–CO and para-NH$_3$–CO complexes.

Accompanying ab initio calculations of the intermolecular potential energy surface (PES) of NH$_3$–CO have been carried out at the explicitly correlated coupled cluster level of theory with single, double and perturbative triple excitations [CCSD(T)-F12a] and an augmented correlation-consistent triple zeta (aVTZ) basis set. The global minimum of the five-dimensional PES corresponds to an approximately T-shaped structure with the N atom closest to the CO subunit and binding energy $D_e = 359.21$ cm$^{-1}$. The bound rovibrational levels of the NH$_3$–CO complex were calculated for total angular momentum $J = 0$ to 6 on this intermolecular potential surface and compared with the experimental results. The calculated dissociation energies $D_0$ are 210.43 and 218.66 cm$^{-1}$ for ortho-NH$_3$–CO and para-NH$_3$–CO, respectively.

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RELEASE OF THE MOGADOC UPDATE WITH AN ENHANCED 3D-VIEWER

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On previous colloquia of this conference series several improvements of the MOGADOC database (Molecular Gas-phase Documentation) were already reported. In the meantime the database has grown up to about 11,500 inorganic, organic, and organometallic compounds, which were studied in the gas-phase mainly by microwave spectroscopy, radio astronomy and electron diffraction. For about 9,200 compounds the structural parameters such as internuclear distances, bond and dihedral angles are given numerically, which have been excerpted from the literature and critically evaluated, whereas spectroscopic parameters and electric, magnetic and dynamic properties can only be retrieved by keyword search terms.

The retrieval features of the HTML-based database have been described elsewhere. Most of the molecular structures, which are also given as ball-stick-models, can be visualized in three dimensions by a specially developed Java-applet. The new update enables among others as new features the visualization of distances between centroids, distances between atoms and ring planes, angles between ring planes, angles between bonds and principal inertial axes, etc.

The project has been supported by the Dr. Barbara Mez-Starck Foundation, Freiburg (Germany).

EMISSION SPECTROSCOPY OF THE A1Π − X1Σ+ SYSTEM OF THE AlD ISOTOPOLOGUE

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The emission spectrum of the A1Π − X1Σ+ system of AlD has been observed in the 22400−23700 cm⁻¹ spectral region at high resolution using a high accuracy dispersive optical spectroscopy. The AlD molecules were formed and excited in an aluminum hollow-cathode lamp with two anodes, filled with a mixture of Ne buffer gas and a trace amount of ND₃. In total, 133 transitions wavenumbers belonging to the 0–0 and 1–1 bands were precisely measured and rotationally analyzed. The present data have been combined with available high resolution measurements of the ro-vibrational bands by White et al.¹ to provide improved spectroscopic constants for the A1Π, v = 0, 1 state of AlD. With the help of the early results of Holst and Hulthen² the main equilibrium constants of the A1Π state were obtained as follows: νₑ = 23653.8343(15) cm⁻¹, ωₑ = 1015.2849(14) cm⁻¹, ωₓₑ = [86.005] cm⁻¹, Bₑ = 3.239806(45) cm⁻¹, αₑ = 0.127934(55), γₑ = [−0.052] cm⁻¹, Dₑ = 2.91922(76) × 10⁻⁴ cm⁻¹, βₑ = 3.6662(13) × 10⁻⁴ cm⁻¹ and δₑ = [2.11 × 10⁻⁴] cm⁻¹.

PROBING COLLISIONAL RELAXATION DYNAMICS IN CO$_2$ GAS MIXTURES THROUGH FIELD-FREE MOLECULAR ALIGNMENT

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Laser-induced molecular alignment and more generally the spatial manipulation of molecules have stimulating perspectives in fields such as the track of molecular reactions, high-order harmonics generation, strong field molecular processes and laser filamentation, to mention but a few. Experimentally demonstrated more than 10 years ago, the nonresonant interaction between non-spherical molecules and a short and intense laser pulse leads to the production of postpulse transient molecular alignment revivals. When the intensity is high enough, a component known as permanent alignment is also observed. Under dissipative conditions, both transient and permanent components undergo temporal decays with different time constants, due to the different relaxation mechanisms that give rise to them.

On one hand, inelastic collisions result in exchanges of population between rotational states $J$ either by conserving the ratio $M/J$ or not (reorienting collisions). On the other hand, elastic collisions can either reorient the angular momentum or be purely dephasing. Molecular alignment gives therefore a unique and efficient tool for probing within a single measurement, the dynamics of elastic collisions.

In this poster, we summarize the results obtained in the case of pure CO$_2$ and CO$_2$-He mixtures$^1$ as well as in CO$_2$-Ar systems$^2$, at pressures up to 20 bars at room temperature. Measurements were performed with a well-known polarization technique (Raman Induced polarization spectroscopy), where a weak probe pulse measures the transient birefringence resulting from the alignment.

$^2$F. Chaussard et al., J. Raman Spectrosc., first published online : January 2015 DOI: 10.1002/jrs.4646
The analysis is performed with a quantum mechanical density matrix formalism using $J$ and $M$-dependent state-to-state transfer rates.
MIPAS DATABASE: NEW HNO₃ LINE PARAMETERS AT 7.6 MICRONS DERIVED FROM LABORATORY INTENSITY MEASUREMENTS AND MIPAS SATELLITE SPECTRA

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Improved line positions and intensities have been generated for the 7.6 µm spectral region of nitric acid. They were obtained relying on a recent reinvestigation of the nitric acid band system at 7.6 µm and comparisons of HNO₃ concentration profiles retrieved from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) limb emission radiances in the 11 and 7.6 µm domains. This has led to an improved database called MIPAS-4.43. Comparisons with available laboratory information (individual line intensities, integrated absorption cross sections, and absorption cross sections) showed that MIPAS-4.43 provides an improved description of the 7.6 µm region of nitric acid. This study should help to improve HNO₃ satellite retrievals by allowing measurements to be performed simultaneously in the 11 and 7.6 µm micro-windows. In particular, it should be useful to analyze existing IASI spectra as well as spectra to be recorded by the forthcoming Infrared Atmospheric Sounding Interferometer - New Generation (IASI-NG) instrument, developed by CNES.
In spite of its importance in radiative budget and in climate change, very few measurements of the water vapor continuum are available in the near infrared atmospheric windows especially for temperature conditions relevant for our atmosphere. This is in particular the case for the 2.3 and 1.6 \( \mu \text{m} \) windows where the very few available measurements show a large disagreement. This lack of experimental data is directly linked to the difficulty to measure weak broadband absorption signals. We have recently used the Cavity Ring Down spectroscopy technique (CRDS) to measure the water vapor self-continuum cross-sections in the 1.6 \( \mu \text{m} \) transparency window\(^1,2\). The derived self-continuum cross sections, \( C_S(T=296 \text{ K}) \), ranging between \( 3 \times 10^{-25} \) and \( 3 \times 10^{-24} \text{ cm}^2 \text{ molec}^{-1} \text{ atm}^{-1} \) were found much smaller than derived by Fourier Transform Spectroscopy\(^3,4\) and in a reasonable agreement with the last version of the MT-CKD 2.5 model\(^5\), except for the temperature dependence in the center of the window which was found significantly smaller than predicted. We report here new measurements of the water self- and foreign- continua in the 2.3 \( \mu \text{m} \) window, near 4250 and 4300 cm\(^{-1}\), by CRDS and OF-CEAS, respectively. The Optical Feedback Cavity Enhanced Absorption Spectroscopy technique\(^6\) is a high sensitive absorption technique using a high finesse cavity like CRDS. Self-continuum cross-sections were retrieved from the quadratic dependence of the spectrum base line level measured for different water vapor pressures between 0 and 15 Torr, after subtraction of the local water monomer lines contribution calculated using HITRAN2012 line parameters. The \( C_S \) values were determined with an accuracy estimated to 5\%. Their values are found 20\% higher than predicted by the MT-CKD V2.5 model but 2-3 times smaller than reported by FTS. The foreign-continuum was evaluated by injecting various amounts of synthetic air in the CRDS cell.

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while keeping the initial water vapor partial pressure constant. The foreign-continuum cross-section, $C_F$, is larger by a factor of 4.5 compared to the MT-CKD values and smaller by a factor of 1.7 compared to previous FTS values\textsuperscript{7}.

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The rotational spectrum of the NH$_3$–H$_2$ van der Waals complex in a supersonic jet has been measured for the first time. This study is intended to reveal the intermolecular interaction between ammonia and dihydrogen and to test the recent ab initio potential energy surface (PES) calculations$^1,^2$. Detailed knowledge of the NH$_3$–H$_2$ interaction parameters is important for a number of applications in astrophysics.

Three different experimental techniques, namely, molecular beam Fourier transform microwave spectrometer, millimeter-wave OROTRON intracavity jet spectrometer and supersonic jet spectrometer with multipass cell, were used to detect pure rotational transitions in the wide frequency range from 39 to 230 GHz. The hyperfine splitting due to the $^{14}$N nuclear spin of ammonia was observed for the $J = 1 \rightarrow 0$ transitions. The obtained data were analyzed in order to determine the molecular parameters and structure of the oNH$_3$–oH$_2$ and pNH$_3$–oH$_2$ complexes. The experimental results were compared with the bound states calculations$^3$ using earlier reported ab initio interaction potential.

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$^3$A. van der Avoird, private communication (2013).
VARIATIONAL CALCULATION OF SENSITIVITY COEFFICIENTS TO PROBE A VARIABLE PROTON-TO-ELECTRON MASS RATIO

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Molecular spectroscopy is a valuable tool in the search for a possible variation of the proton-to-electron mass ratio $\mu$. A variable $\mu$ would cause observable shifts in the transition frequencies of certain molecules, and this effect can be quantified through the calculation of sensitivity coefficients. We present a new approach to computing sensitivity coefficients which uses the variational nuclear motion code TROVE. Calculations are robust and accurate, and the method is easily transferable to a range of systems. A comprehensive study of the vibration-rotation-inversion transitions of $^{14}$NH$_3$, $^{15}$NH$_3$, $^{14}$ND$_3$, and $^{15}$ND$_3$ has been carried out. Other molecules, such as H$_3$O+, are being investigated to determine promising transitions which can guide future laboratory and astronomical observations.


EXPERIMENTAL AND THEORETICAL STUDYING OF VAN DERWAALS CO$_2$ CLUSTERS FOR PLANETARY ATMOSPHERES MODELLING

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Studying of carbon dioxide clusters is required for radiative transfer modelling of the atmospheres of Mars and Venus due to its high abundance. The atmosphere of Venus consists of more than 96 % of CO$_2$, and about 4 % corresponds to (CO$_2$)$_2$ clusters. Current experimental studies of weakly bound van der Waals CO$_2$ complexes are mainly performed in supersonic molecular jets\(^1\) and recording of gas spectra at atmospheric pressure\(^2\). With increasing gas pressure dimer band shape is transformed and this evolution is a proper source of information on the dynamics and stability of dimers knocked by surrounding molecules.

In our work for the first time we used a high resolution molecular spectroscopy for studying dimer absorption at high gas pressure. Also we provided realistic theoretical modelling of the band shape transformation with increasing pressure. We obtained that the shape of CO$_2$ dimer bands is influenced by the line-mixing effects\(^3\), what demonstrate an unexpected stability of the dimers despite the collisions with bath molecules and negates the common belief that CO$_2$ dimers are shot-lived complexes. The simple strong collision model\(^4\) is used to describe the band shape in a qualitatively correct manner. Our results are expected to improve the modelling of CO$_2$-rich atmospheres and provide also a new spectroscopic tool for studying of the stability of molecular clusters.

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A NEW LINELIST FOR HOT VO: CHALLENGES AND PROGRESS

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Diatomic vanadium oxide (VO) is an astrophysically important molecule responsible for significant near-IR and visible absorption in M-type stars where it has abundance from about 1500 K to 3000 K. A line list containing the frequencies and intensities required to model the full visible and infrared rovibronic absorption spectrum, ideally up to 5000 K for coverage, is highly desired for modelling the properties and spectroscopy of cool stellar and hot planetary atmospheres; this is being produced as part of the ExoMol project. VO has three allowed transitions from the ground state ($A^4\Pi \leftarrow X^4\Sigma^-$, $B^4\Pi \leftarrow X^4\Sigma^-$ and $C^4\Sigma^+ \leftarrow X^4\Sigma^-$); however, at 5000K, there is significant population in the first few excited states ($a^2\Sigma^-$, $A'^4\Phi$, $b^2\Delta$ and $A^4\Pi$) from which transitions should ideally be included. There is also significant spin-orbit coupling between states, which will lead to some intensity in spin-forbidden transitions. Current ab initio electronic structure theory calculations are not spectroscopically accurate; however, they are the only current source of intensity information (i.e. diagonal and off-diagonal dipole moments) as well as the primary source of spin-orbit coupling data. Techniques including using minimal and different CASSCF spaces, finite field dipole moments and multi-reference configuration interaction are utilised to maximise the accuracy of the theoretical calculations. The newly developed variational nuclear motion problem for coupled electronic surfaces in diatomics, Duo, is used to produce the full rovibronic energy levels and transition data for VO. The parameters of the potential energy surfaces and coupling curves are optimised to fit experimental energy levels. Experimentally derived empirical diagonal spin-spin and spin-rotation terms are shown in some cases to arise from off-diagonal spin-orbit and electronic angular momentum coupling, in particular for the ground state. Finally, the theoretical dipole moment curves are utilised to produce the final line list to be tested in astrophysical models.
HIGH RESOLUTION ANALYSIS OF THE $\nu_1$ AND $\nu_5$ BANDS OF PHOSGENE $^{35}$Cl$_2$CO AND $^{35}$Cl$^{37}$ClCO

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Phosgene is relatively more abundant in the stratosphere, where it has a lifetime of several years, but is also present in the troposphere in spite of a shorter lifetime (seventy days). Thus, monitoring its concentration by remote sounding of the upper atmosphere is of importance, all the more so that some of its strong infrared absorptions, occurring in the important 8-12 $\mu$m atmospheric window, hinder the correct retrieval of Freon-11 concentration profiles. Indeed, the useful infrared absorptions of this compound, a reference for ozone depleting substances, occur in the same spectral region. The present lack of accurate spectral information is indeed a serious obstacle, not only for measuring the abundance of phosgene in the atmosphere, but also because our inability to model and remove phosgene’s prolific signature in many infrared spectral regions is a major hindrance to the search for the signatures of new stratospheric trace species. Therefore, Doppler-limited resolution spectra of phosgene (Cl$_2$CO) have been recorded at 169 K in the 11.75 and 5.47 $\mu$m spectral regions using a Bruker IFS125HR spectrometer on the AILES Beamline at SOLEIL, leading to the observation of the fully resolved $\nu_1$ and $\nu_5$ vibrational bands of the two isotopologues $^{35}$Cl$_2$CO and $^{35}$Cl$^{37}$Cl. The corresponding upper state ro-vibrational levels were fitted using Watson-type Hamiltonians and/or a Hamiltonian matrix accounting for resonance effects when necessary. In this way, it was possible to reproduce the upper state ro-vibrational levels to within the experimental accuracy, i.e. 0.00017 cm$^{-1}$. Very accurate band centers, rotational, centrifugal distortion and coupling constants have thus been determined. Phosgene, however, presents four fundamentals in the far infrared region below 600 cm$^{-1}$, with the lowest ($\nu_3$) near 285 cm$^{-1}$. These

are responsible for hot bands, not yet analysed but of great importance for the correct retrieval of Freon-11 atmospheric absorption profiles. In a second study which is in progress we will record and analyze the fundamentals in the 200 - 600 cm$^{-1}$ spectral region in order to provide the sets of spectroscopic parameters essential for the precise modelling of phosgene absorptions in the infrared atmospheric windows.
Stable bimolecular complexes (tightly bound dimers) in the gas phase are usually formed in the course of third body stabilization of their unstable precursors - metastable dimers (also called as quasibound complexes (QC), or collision complexes). The latter can form provided at least one of colliding partners has internal degree of freedom (see, e.g. [1] and references therein). Methane (CH$_4$) is very important molecule in our environment: it is the main component of natural gas; it is (along with H$_2$O and CO$_2$) responsible for the greenhouse effect and global warming in the atmosphere. Also CH$_4$ is one of key components of some of the outer planets (Saturn, Jupiter) and their moons (Titan). In this work, CH$_4$-Ar, CH$_4$-Ne and CH$_4$-He collision complexes are studied by means of classical dynamics. CH$_4$ molecule is treated as a rigid spherical top; 9 exact three-dimensional (3D) classical Hamilton equations in action-angle variables are used to simulate collisions; Monte Carlo procedure is used to select initial conditions. Intermolecular interactions are modeled by simple but realistic 3D potentials (distance + two angles): CH$_4$-Ar [2], CH$_4$-Ne [3], and CH$_4$-He [4]. Rotational state-to-state relaxation cross sections of CH$_4$ are calculated and compared with available data. Statistical analysis is made for the parameters of QC formed in collisions. It is observed that metastable dimers of methane may be both short-lived and very long-lived and characterized by a variety of interparticle separations. The following statistical distributions of QC are derived from trajectories: life-time, number of closest approaches, distances of the closest and farthest approaches. The cross sections of QC formation as a function of temperature are obtained and analysed.

REFERENCES
AB INITIO VARIATIONAL PREDICTIONS FOR HIGH-RESOLUTION LASER SPECTROSCOPY: ASSIGNMENT OF 107 NEW SUB-BANDS OF METHANE IN THE ICOSAD RANGE 6280-7800 CM$^{-1}$

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A detailed study of methane spectra in the highly congested icosad range 6280-7800 cm$^{-1}$ has been performed using variational global calculations derived from accurate ab initio potential energy and dipole moment surfaces. For the very first time, the experimental WKLMC line lists—recorded at 80 and 296 K using very sensitive laser techniques (DAS, CRDS) and considered as the most significant advance in methane spectroscopy in the near infrared—have been partly assigned from first principles predictions. Among the 20 bands and the 134 sub-levels contain in the icosad system, 19 and 107, respectively, have been identified for line intensities $I \geq 10^{-27}$ cm/molecule. Finally a total of 12900 transitions and 7300 energy levels was assigned, which represent about 20% of the experimental list at 80 K. This gives approximately 98, 85, 62 and 50% of assigned lines for measured intensities $I \geq 10^{-23}$, $I \geq 10^{-24}$, $I \geq 10^{-25}$ and $I \geq 10^{-26}$ cm/molecule, respectively. This work clearly demonstrates the validity of our recent global calculations. It could be used in various applications, as the generation of accurate high-temperature line lists. Simultaneously, the modeling of the methane spectra at 80K in the 6539-6800 cm$^{-1}$ region is currently in progress and should allow to validate the global assignments. This

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AN INTENSITY STUDY OF THE TORSIONAL BANDS OF ETHANE AT 35 MICRON

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Ethane is the second most abundant hydrocarbon detected in the outer planets. Although the torsional mode is not infrared active in lowest order, the strongest feature in this band can be seen near 289 cm$^{-1}$ in the CASSINI CIRS spectrum of Titan. Prior laboratory studies have characterized the torsional frequencies to high accuracy and measured the intensities to temperatures as low as 208 K. However, for the interpretation of the far-infrared observations of Titan, further investigation was needed to determine the intensities at lower temperatures and to higher accuracy. The spectrum of C$_2$H$_6$ was investigated from 220 to 330 cm$^{-1}$ to obtain the band strengths of the torsional fundamental $\nu_4$ (near 289 cm$^{-1}$) and the first torsional hot band $2\nu_4 - \nu_4$. Seven laboratory spectra were obtained at resolutions of 0.01 and 0.02 cm$^{-1}$ using a Bruker IFS-125 Fourier transform spectrometer at the Jet Propulsion Laboratory. The interferometer was coupled to a coolable multi-pass absorption cell set to an optical path length of 52 m. The range of temperatures was 166 to 292 K with the lower temperatures being most relevant to the stratosphere of Titan. The ethane sample pressures ranged from 35 to 254 Torr. The modeling of the transition intensities required the expansion of the dipole moment operator to higher order; this introduced Herman-Wallis like terms. The fitting process involved five independent dipole constants and a single self-broadening parameter. The results presented should lead to an improved understanding of the methane cycle in planetary atmospheres and permit other molecular features in the CIRS spectra to be identified.
RELATIVISTIC DEFORMATION OF SPECTROSCOPIC LINE SHAPES

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Usually a nonrelativistic transformation from the molecule frame to the lab frame as well as nonrelativistic velocity distribution is assumed for the purpose of the modeling of spectroscopic line shapes. However recent developments in ultrahigh signal-to-noise-ratio line-shape measurements inspire to ask the question about the possibility of the relativistic effects observation in the shapes of molecular spectra.

We developed a relativistic formulation of the Voigt profile for the case of spontaneous emission\(^1\). We have shown that our formula has a proper asymptotic behavior in the cases of the classical Voigt profile and the relativistic Gauss profile\(^2\). Moreover we presented analytically that our profile is normalized and we gave an alternative expression, which allows our profile to be numerically evaluated for the weak-relativistic regime, which is physically the most meaningful. Finally we estimated that at room temperature the relative amplitude of the relativistic correction can be higher than \(10^{-6}\).

ANALYSIS OF HIGH RESOLUTION RO-VIBRATIONAL SPECTRUM OF THE CH$_2$=CHD MOLECULE IN THE REGION OF 2800 – 3300 CM$^{-1}$: THE $\nu_2 + \nu_3$, $\nu_2 + \nu_{12}$, $\nu_1$, $\nu_5$, $\nu_7 + \nu_{11}$ AND $\nu_9$ BANDS

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The CH$_2$=CHD molecule is an asymmetric top molecule with a symmetry isomorphic to the C$_s$ point symmetry group. In present study we consider the following fundamental and combinational ro-vibrational bands: $\nu_2 + \nu_3$ ($A'$), $\nu_2 + \nu_{12}$ ($A'$), $\nu_1$ ($A'$), $\nu_5$ ($A'$), $\nu_7 + \nu_{11}$ ($A''$) AND $\nu_9$ ($A'$), which are located in the region of 2800 – 3300 cm$^{-1}$.

The high resolution spectrum was recorded using Brucker 120HR Fourier spectrometer at Nanyang Technological University in Singapore with isotopically pure sample of CH$_2$=CHD. Estimated experimental uncertainty of line position is 2-3 $\times 10^{-4}$ cm$^{-1}$. The effective Hamiltonian model, which takes into account Coriolis and Fermi resonance interactions between all studied vibrational states was used. The set of spectroscopic parameters obtained from the fit procedure reproduces the initial experimental data with an accuracy close to experimental uncertainties.
Invited Lectures G

Tuesday, August 25, 14:00

Chair : J. U. GRABOW
CAVITY-ENHANCED FREQUENCY COMB SPECTROSCOPY

(45 min.)

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With our recent development of novel frequency combs in the mid infrared and extreme ultraviolet, we have opened the door for sensitive and high-resolution spectroscopy in these spectral regions. Cavity-enhanced direct frequency comb spectroscopy provides simultaneous and precise measurements of many types of molecules, analyzing their spectral strengths and patterns, and thus forming global, signatory identifications of trace presence at an unprecedented level of specificity and confidence. With the integration of a powerful capability for time-resolved transient absorption at high spectral resolution, we demonstrate the utility of this technique for identifying transient chemical species and studying reaction kinetics. Combined with the technology of cold molecules, we can unravel complex spectra from large molecules and obtain new insights to molecular structure and dynamics. Finally, with an XUV comb produced inside an enhancement cavity we can directly manipulate molecules and probe the extreme nonlinear physics, opening future high-precision measurements in strong-field phenomena.
The spectrum of molecular hydrogen H$_2$ can be measured in the laboratory to very high precision using advanced laser and molecular beam techniques, as well as frequency-comb based calibration. The quantum level structure of this smallest neutral molecule can now be calculated to very high precision, based on a very accurate Born-Oppenheimer potential and including subtle non-adiabatic, relativistic and quantum electrodynamic effects. Comparison between theory and experiment yields a test of QED, and in fact of the Standard Model of Physics, since the weak, strong and gravitational forces have a negligible effect. Even fifth forces beyond the Standard Model can be searched for. Astronomical observation of molecular hydrogen spectra, using the largest telescopes on Earth and in space, may reveal possible variations of fundamental constants on a cosmological time scale. A study has been performed at a look-back time of 12.5 billion years. In addition the possible dependence of a fundamental constant on a gravitational field has been investigated from observation of molecular hydrogen in the photospheres of white dwarfs. The latter involves a test of the Einstein's equivalence principle.
Poster Session H

Tuesday, August 25, 16:00
ROUTINE CAVITY RING DOWN SPECTROSCOPY WITH SUB-MHZ ABSOLUTE FREQUENCY CALIBRATION

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Continuous Wave Cavity Ring Down Spectroscopy is a rather simple and elegant method to reach very high detection sensitivities, e.g. $\sim 5 \times 10^{-13} \text{ cm}^{-1}$. In the frequency domain, the ring down event (RD) presents the advantage of evolving independently of the excitation laser source, which is interrupted. Therefore, if the laser frequency is determined correctly when the RD is triggered, the latter can be accurately frequency stamped.

We present here an original on the fly absolute frequency determination scheme that uses both a precise Fizeau wavemeter (5 MHz precision, 20 MHz accuracy) and an Optical Frequency Comb (OFC). We show that the short response time and accuracy of the former is sufficient to unambiguously determine the exact OFC mode in resonance with the probe laser at RD trigger time. Therefore, the OFC measurement accuracy (potentially Hz level) is fully transferred to wavemeter readings. We demonstrate that the infrared emission frequency of telecom DFB lasers can be determined with an accuracy better than 1 MHz RMS within 2 $\mu$s. The performances of the method are illustrated on isolated line profiles of C$_2$H$_2$ and broadband spectra of CO, C$_2$H$_2$ and D$_2$ recorded with this frequency-stamp method near 1.5 $\mu$m. Line positions are determined with an accuracy better than 300 kHz, without any impact on the original cw-CRDS instrument scanning speed or sensitivity performances.

An alternative CRDS measurement scheme, involving loose lock of the DFB laser to one specific OFC mode is also described. It permits to further improve the instrument sensitivity and apparatus function. Such an approach would take a large benefit of a narrower laser linewidth.


We present the Optical Feedback Frequency-Stabilized Cavity Ring-Down spectrometer that allows recording accurate absorption spectra over 1 THz in the infrared telecom region (∼1.6 µm) with 1 kHz resolution. It combines a highly stable optically locked source, a finely radio-frequency tunable optical single-sideband modulator and a tightly Pound-Drever-Hall locked cavity ring-down spectrometer. This arrangement allows (1) the high stability of the source to be transferred to the ring-down cavity, (2) an optimal coupling of the laser leading to nearly shot-noise-limited ring-down measurements to be achieved, (3) intracavity power at the kW/cm² level to be reached, leading to well-marked saturated absorption features even for weak transitions. We demonstrate a single ring-down event precision of $3 \times 10^{-12}$ cm$^{-1}$, a sensitivity of $2 \times 10^{-13}$ cm$^{-1}$Hz$^{-1/2}$, a spectrum noise floor of $9 \times 10^{-14}$ cm$^{-1}$ after 24 h averaging on a spectral interval of 10 MHz.

To illustrate the performance of the instrument, single-line and broadband molecular spectra are presented and analyzed using advanced line profiles. Moreover, taking the saturated absorption during the ring-down decay in a TEM$_{00}$ field into account, an analytical expression for the non-exponential ring-down signal, in the limit of low saturation, has been derived. This formula leads to an explicit decoupling of saturation effects - including Lamb dip features - from the unsaturated absorption coefficient, in particular opening the door to concentration-independent measurements of transition dipole moments. An example is shown in the case of a weak CO$_2$ transition near 1.6 µm.
HIGH SENSITIVITY CW-CAVITY RING DOWN SPECTROSCOPY OF N$_2$O NEAR 1.22 µm

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The absorption spectrum of nitrous oxide (N$_2$O) in natural isotopic abundance has been recorded with a highly sensitive CW-Cavity Ring Down Spectrometer. The room temperature recordings were performed with a pressure of 10 Torr in the 7915-8334 cm$^{-1}$ spectral range (1.26-1.19 µm). The achieved sensitivity, noise equivalent absorption $\alpha_{\text{min}} \approx 3 \times 10^{-11}$ cm$^{-1}$, allowed for the detection of lines with intensity smaller than $5 \times 10^{-29}$ cm/molecule. More than 3200 transitions belonging to 66 bands of five isotopologues (N$_{14}$N$_{16}$O, N$_{15}$N$_{14}$N$_{16}$O, N$_{14}$N$_{15}$N$_{16}$O, N$_{14}$N$_{217}$O, N$_{14}$N$_{218}$O) have been rovibrationally assigned on the basis of the predictions with the effective Hamiltonian models 1, 2, 3. For comparison, only 12 bands were previously measured by Fourier Transform spectroscopy in the studied region. All identified bands belong to the $\Delta P=13$ and 14 series of transitions, where P=2$V_1$+V$_2$+4$V_3$ is the polyad number ($V_i$ are vibrational quantum numbers). The line positions and intensities have been measured for all assigned lines. The band-by-band analysis has allowed deriving accurate spectroscopic parameters from a fit of the measured line positions. The typical rms value of the ($\nu_{\text{obs}} - \nu_{\text{fit}}$) differences is $0.6 \times 10^{-3}$ cm$^{-1}$. The global modeling of the line positions was performed to refine the corresponding set of the effective Hamiltonian parameters of the N$_{14}$N$_{218}$O isotopologue. A few resonance perturbations were identified.

THE MILLIMETER-WAVE SPECTRA OF METHACROLEIN AND METHYL VINYL KETONE. TORSION-ROTATION-VIBRATION EFFECTS IN THE EXCITED STATES

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Isoprene, and its major oxidation products methacrolein (MAC), \( \text{CH}_2=\text{C} (\text{CH}_3) \text{CHO} \), and methyl vinyl ketone (MVK), \( \text{CH}_3 \text{C} (\text{O}) \text{CH}=\text{CH}_2 \), are the primary contributors to annual global volatile organic compounds (VOCs) emissions. We report the analysis of the rotational spectra of MAC and MVK recorded in the 50 - 650 GHz region using the Lille spectrometer. The spectroscopic characterization of MAC/ MVK ground state will be useful in the detailed analysis of high resolution infrared spectra. Both MAC and MVK contain one internal rotor, the methyl group, that exhibits large amplitude torsion with respect to their molecular frames. In the Doppler-limited spectra the splittings due to the internal rotation of methyl group were resolved. In order to account for these splittings we used the Rho-Axis-Method Hamiltonian and RAM36 code to fit the rotational transitions. Our study is supported by high level quantum chemical calculations to model the structure of both molecules and to obtain the harmonic force field parameters, internal rotation barrier heights, and vibrational frequencies. At room temperature conditions, in the recorded spectra along with the ground state lines we assigned several low-lying excited vibrational states. The analysis of these states revealed different rotation-vibration interactions: Fermi and Coriolis - type coupling, as well as kinetic coupling between the skeletal and methyl torsional modes. In particular, the kinetic coupling is responsible for the inverted sequence of A-E tunneling substates and anomalously high A-E splittings in the first excited vibrational state of skeletal torsion.

Support from the CaPPA project (Chemical and Physical Properties of the Atmosphere) is acknowledged. CaPPA is funded by the French National Research Agency (ANR) through the PIA (Programme d’Investissement d’Avenir) under contract ”ANR-11-LABX-0005-01” and by the Regional Council ”Nord-Pas de Calais” and the ”European Funds for Regional Economic Development (FEDER).”
HIGH RESOLUTION HETERODYNE DETECTION REVEALS THE DISCRETE NATURE OF COHERENT SYNCHROTRON EMISSION AS A HIGH DENSITY FREQUENCY COMB THZ SOURCE

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Frequency combs have enabled significant progress in frequency metrology and high-resolution spectroscopy extending the achievable resolution while increasing the signal to noise ratio. In its coherent mode, synchrotron radiation is accepted to provide an intense THz continuum covering a wide spectral range from about 0.1 to 1 THz. Using a dedicated heterodyne receiver, we reveal the purely discrete nature of this emission. A phase relationship between the light pulses leads to a powerful frequency comb spanning over one decade in frequency. The comb has a mode spacing of 846 kHz, a linewidth of about 200 Hz, a fractional precision of about $2 \times 10^{-10}$ and no frequency offset. We performed a preliminary high resolution measurement on acetonitrile as a proof of principle of the set-up.

We will present the technical details of the heterodyne receiver and the characteristics of the THz frequency comb obtained in low-alpha, 8 bunches, and single bunch machine operation modes.

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SPECTROSCOPY OF $^{14}$NH$_3$ IN THE 2.3 MICRON RANGE:
ASSIGNMENTS OF HOT BANDS

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Using a VECSEL (Vertical External Cavity Surface Emitting Laser) source, $^{14}$NH$_3$ spectra have been recorded at different temperatures and pressures in the range 4275 to 4356 cm$^{-1}$ (2295-2339 nm). 664 transitions have been discriminated belonging to $^{14}$NH$_3$. The lower state energy of the transitions has been derived for 572 transitions. With this new information, a comparison have been done with the calculated line list of Yurchenko et al$^1$. An assignment is proposed for 563 components which significantly increases the information of the HITRAN 2012 database (238 transitions present in this range). Considering the energy position, the intensity and the lower state energy, these assignments have been tested with the help of 3D graphical plot considering the tendency of the observed - calculated difference within combination bands. The method includes the GSCD technique (Ground State Combination Difference). 94 transitions of the combination $\nu_2 + 2\nu_4$ have been found (only one present in HITRAN) as well as for the first time 77 transitions of the hot band $2\nu_2 + \nu_3 - \nu_2$.

HIGH RESOLUTION ANALYSIS OF S\textsuperscript{18}O\textsubscript{2} AND S\textsuperscript{16}O\textsuperscript{18}O SPECTRUM: THE $\nu_1$ AND $\nu_3$ INTERACTING BANDS

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High resolution ro-vibrational spectra of the S\textsuperscript{18}O\textsubscript{2} and S\textsuperscript{16}O\textsuperscript{18}O molecules were recorded with a Bruker IFS 120 HR Fourier transform interferometer in the region of 1030 - 1400 cm\textsuperscript{-1}, where the bands $\nu_1$ and $\nu_3$ of both species are located, and theoretically analyzed.

The weighted fit of the assigned transitions was made with the Hamiltonian model which takes into account Coriolis resonance interaction between the vibrational states (100) and (001). To make the ro-vibrational analysis physically more suitable, the initial values of the main spectroscopic parameters have been estimated from the values of the corresponding parameters of the S\textsuperscript{16}O\textsubscript{2} species on the basis of the Isotopic Substitution theory results.

Finally, the sets of spectroscopic parameters were obtained for both, S\textsuperscript{18}O\textsubscript{2} and S\textsuperscript{16}O\textsuperscript{18}O, species. Also, the rotational structure of the ground vibrational state of the S\textsuperscript{18}O\textsubscript{2} molecule has been improved in comparison with the results of Ref. [1].

References
A HIGH RESOLUTION ANALYSIS OF 2ν₂/ν₂+ν₄/2ν₄ BANDS OF $^{M}$GeH₄ (M=76,74)

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High resolution analysis of the GeH₄ spectra was made for doubly excited deformation vibrational bands, 2ν₂/ν₂+ν₄ and 2ν₄. The infrared spectrum of GeH₄ (88.1% of $^{76}$GeH₄, 11.5% of $^{74}$GeH₄, and a minor amounts of three other stable isotopic species in the sample) was recorded in the region of 1350 - 2300 cm⁻¹ with a Bruker IFS 125HR Fourier transform spectrometer (Nizhny Novgorod, Russia) and analyzed. Assigned line positions of discussed bands were used then in a fit procedure. Rotational, centrifugal distortion, and resonance interaction parameters were determined. Obtained from the fit set of spectroscopic parameters reproduces the initial experimental data within accuracy close to experimental uncertainties.
DISPERSED FLUORESCENCE SPECTROSCOPY OF THE $\tilde{B} 2E' - \tilde{X} 2A'_2$ TRANSITION OF $^{14}$NO$_3$ and $^{15}$NO$_3$

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The laser induced fluorescence (LIF) spectrum of the $\tilde{B} 2E' - \tilde{X} 2A'_2$ transition was obtained for $^{14}$NO$_3$ and $^{15}$NO$_3$ generated by pyrolysis of $^{14}$N$_2$O$_5$ and $^{15}$N$_2$O$_5$, respectively, under supersonic free jet expansion. The positions of the $e'$ vibronic bands observed in the dispersed fluorescence (DF) spectra from single vibronic levels (SVL’s) for both isotopomers are completely consistent with the band origins of the high-resolution IR absorption spectra$^1$. Other vibronic bands of the $^{14}$N species not observed in the IR spectra, also show good agreement with reported dispersed fluorescence spectra under room temperature conditions$^2$. These should be attributed to the bands terminating to the $a'_1$ vibrational levels in the $\tilde{X} 2A'_2$ state. An important finding in this DF experiment is that all of the vibronic bands, except one, show usual isotope shift, i.e. $\nu(14\text{NO}_3) > \nu(15\text{NO}_3)$. The exception is the $\nu_1$ fundamental at 1051 and 1053 cm$^{-1}$ for the $^{14}$NO$_3$ and $^{15}$NO$_3$ isotopomers, respectively, which shows inverse isotope shift, $\nu(14\text{NO}_3) < \nu(15\text{NO}_3)$. Our higher resolution DF spectra of the $\nu_1$ fundamental region show there is an additional vibronic band at 1056 and 1039 cm$^{-1}$ for the $^{14}$N and $^{15}$N isotopomers, respectively. We interpreted this inverse isotope shift of the $\nu_1$ fundamental to be cause by Fermi-type interaction with this newly observed band, and concluded that the new band should be attributed to a band fluorescent to an $a'_1$ vibrational level of the $\tilde{X} 2A'_2$ state. We attributed this new band as one terminating to the 3 $\nu_1 (a'_1)$ over-tone vibrational level with a 17 cm$^{-1}$ isotope shift. High-resolution IR absorption spectroscopy identified the 1173 and 1161 cm$^{-1}$ bands for the $^{14}$N and $^{15}$N isotopomers, respectively, as the $e'$ level of the third over-tone, 3 $\nu_4$, and the present DF work confirms this $e'$ assignment. In addition to the $e'$ level, this work assigns the 1216 and 1200 cm$^{-1}$ bands to the $a'_2$ band of the third over-tone for the $^{14}$N and $^{15}$N species, respectively. Accordingly, the structure of the 3 $\nu_4$ over-tone vibrational level has two characteristics unusual for non-degenerate $2A'_2$ electronic states (though this structure is understandable as one caused by Renner-Teller interaction in degenerate $2E'$ electronic states): (1) unexpectedly wide splitting of the 3

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$^3$K. Kawaguchi, private communication.
ν₄ (a'₁) and (a'₂) levels, \( \sim 160 \text{ cm}^{-1} \), and (2) relative strong intensity, i.e. the intensity of the 3 ν₄ (a'₁) band is comparable with that of the ν₁ fundamental. The unusual vibrational structure and the unexpected band intensities of the 3 ν₄ over-tone as that on a non-degenerate electronic state may be attributed to vibronic coupling and intensity borrowing from the 0₀ band, respectively.
ABSORPTION SPECTRUM OF WATER VAPOR IN THE 3-5 MICRONS TRANSPARENCY WINDOW

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The absorption spectrum of natural water vapor is recorded in the 3-5 µm transparency window using Bruker IFS 125HR FTIR spectrometer coupled with multipass gas cell with optical path length of 1065.5 m. (IAO, Tomsk). The measurement was performed at resolution of 0.01 cm$^{-1}$ and at temperature of 12.5 C. The water vapor pressure was 8.2 mbar. The minimal detectable absorption coefficient $k_v$ is 1x10$^{-9}$ cm$^{-1}$. About 160 weak water absorption lines between 2390 and 2570 cm$^{-1}$ are assigned, more than 100 of them are newly observed. Measured line intensities are compared both with available experimental data and calculated intensities included in the HITRAN2012 and GEISA2014 databases. Disagreements between the experimental and calculated$^{1,2}$ intensities are discussed.


HIGH-RESOLUTION SPECTROSCOPY AND ANALYSIS OF VARIOUS BANDS OF CF$_4$ TO ELUCIDATE ITS HOT BAND STRUCTURE

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We have recorded spectra of the $\nu_2 + \nu_3$ combination band of CF$_4$ under two different physical conditions. i) Jet-cooled spectra with a rotational temperature of ca. 50 K, recorded thanks to the Jet-AILES$^1$ apparatus of the AILES Beamline at the SOLEIL Synchrotron facility. ii) Room-temperature spectra recorded in Reims with a 8 m optical path in a multiple-pass White cell. We present a preliminary analysis of these spectra realized thanks to the XTDS software$^2$. The assignments are included into a global fit implying several interacting bands previously studied$^3$.

We could also record high-resolution spectra of the forbidden $\nu_2$ fundamental band and of the $\nu_1 + \nu_3$ combination band. Our final aim is to obtain a global analysis of all the lower vibrational bands of CF$_4$ and to simulate its hot bands in the atmospheric absorption region.

Experimental and simulated room-temperature spectrum of the $R(47)$ and $R(48)$ line clusters of the $\nu_2 + \nu_3$ band of CF$_4$. 
MODELING OF THE TRIAD \((\nu_8, \nu_1, \nu_6)\) AND THE \(\nu_2\) BAND OF SULFURYL FLUORIDE USING THE \(C_{2v}\) TOP DATA SYSTEM (\(C_{2v}\) TDS) : FREQUENCY ANALYSIS

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Sulfuryl fluoride \(\text{SO}_2\text{F}_2\) was first mentioned in the context of determining the influence of sulfur compounds in the stratosphere\(\textsuperscript{1}\) and it has recently emerged as an important air pollutant\(\textsuperscript{2}\). It is used increasingly as a fumigant of timber, buildings and construction materials. \(\text{SO}_2\text{F}_2\) is used also in agriculture and food processing as a replacement for \(\text{CH}_3\text{Br}\).

Modeling the absorption spectrum is thus essential both for atmospheric concentration measurements, but also for theoretical interests, since \(\text{SO}_2\text{F}_2\) is close to a spherical rotor. A tensorial formalism adapted to \(XY_2Z_2\) asymmetric tops and \(C_{2v}\) symmetry has been developed by M. Rotger et al.\(\textsuperscript{3}\).

In this work, we present the first results of our analysis for the triad \((\nu_8, \nu_1, \nu_6)\). The absorption spectra of the \(\nu_1\) and \(\nu_6\) bands ranging from 1200 to 1800 cm\(^{-1}\) have been recorded at room temperature \((T = 296 \text{ K})\) and for different pressures up to 30 Torr using a high-resolution Fourier transform spectrometer at the GSMA Laboratory. The analysis is currently in progress after having :
- determined the rotational and the Coriolis constants of \(\nu_1\) and \(\nu_6\) with the \textit{ab initio} MP2/cc-pV(T+d)Z method\(\textsuperscript{4}\).
- recorded the spectrum of the \(\nu_8\) band at the AILES beamline of SOLEIL synchrotron.

We also present the first results of our analysis for the \(\nu_2\) band. The absorption spectra of this band centered at 850 cm\(^{-1}\) have been recorded at room temperature \((T = 296 \text{ K})\) at the SOLEIL synchrotron. Knowing that the rovibrational spectra of \(\nu_2\) band have been previously analyzed using a Watson type Hamiltonian\(\textsuperscript{5}\).

\textsuperscript{1}P. Crutzen, \textit{Geophysical Research Letters} \textbf{3}, 73-76 (1976)
\textsuperscript{2}J. Mühle \textit{et al.}, \textit{Journal of Geophysical Research} \textbf{114}, D05306 (2009)
\textsuperscript{4}M.J. Frisch \textit{et al.}, Gaussian 09, Revision A.02 ; Gaussian, Inc., Wallingford, CT (2009)
\textsuperscript{5}I. Merke \textit{et al.}, \textit{Journal of Molecular Structure} \textbf{795}, 185-189 (2006)
A COMBINED GIGAHertz AND TERAHertz SYNCHROTRON-BASED FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDY OF PHENOL AND META- AND ORTHO-D-PHENOL: PROBING TUNNELING SWITCHING DYNAMICS

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Tunneling switching is of fundamental interest for certain experiments aiming at detecting parity violation in chiral molecules. A particularly intriguing recent development is the theoretical prediction of prototypical tunneling switching in meta- and ortho-D-phenol (C₆H₄DOH) as opposed to phenol (C₆H₅OH) where only tunneling dominates the dynamics: For meta and ortho-D-phenol at low energy, tunneling is completely suppressed due to isotopic substitution, which introduces an asymmetry in the effective potential including zero point vibrational energy in the lowest quasiadiabatic channel. This effectively localizes the molecular wavefunction at either the syn or anti structure of meta- and ortho-D-phenol. At higher torsional states of meta- and ortho-D-phenol, tunneling becomes dominant, thus switching the dynamics to a delocalized quantum wavefunction. We have measured and analyzed the rotational spectra of meta- and ortho-D-phenol in the range of 60 to 110 GHz, using an experimental setup which we have improved somewhat, and their rotationally resolved THz and IR spectra in the range of 200 to 1000 cm⁻¹ by synchrotron-based FTIR spectroscopy. Here we shall discuss in detail the GHz spectra of meta- and ortho-D-phenol, which were previously studied only by microwave spectroscopic analyses of the ground vibrational state. We were able to assign and analyze the ground state of the syn and anti isomers of meta- and ortho-D-phenol up to J=35. For meta-D-phenol, assignments of the rotational transitions of the excited torsional states based on the analysis of rovibrational spectra recorded at the synchrotron-based infrared beamline at Swiss Light Source (SLS) will be discussed as well.

5S. Albert, Ph. Lerch, R. Prentner and M. Quack, 68th International Symposium on Molecular Spectroscopy, Columbus, Ohio, USA, June 17-21, paper TG09 (2013).
THEORETICAL REIMS-TOMSK SPECTROSCOPIC LINE LISTS (THEORETS) FOR MOLECULES OF PLANETOLOGICAL AND ASTROPHYSICAL INTEREST

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Knowledge of intensities of rovibrational transitions of various molecules in wide spectral and temperature ranges is essential for the modeling of planetary atmospheres, brown dwarfs, and for other astrophysical applications. This demonstrates the necessity of having adequate and reliable molecular line lists. The TheoReTS project aims at providing complete and comprehensive lists of transitions based on accurate ab initio and variational calculations for a large variety of highly symmetric molecular species as methane, phosphine, ethylene, etc. Calculations on new molecular systems as GeH₄, SiH₄ or CH₃X (X=F, Li, Br, Cl, I) are currently in progress and will be also included in TheoReTS. The development of the TheoReTS website with a dedicated user-friendly graphical interface in frame of Tomsk-Reims collaboration is in progress.

This work is supported by French-Russian LIA SAMI and Tomsk State University Mendeleev grant program.

A DEUTERATED WATER ISOTOPOLOGUE DATABASE TO AID LABORATORY MEASUREMENTS AND MARS ORBITER MISSIONS

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There is a need for measurements of HDO broadened by CO$_2$ to interpret Mars data from the Mars Reconnaissance Orbiter onboard the Mars Climate Sounder and future data from the Trace Gas Orbiter of the ESA ExoMars mission. In these measurements the presence of doubly deuterated water, D$_2$O, must be accounted for to reduce the spectra. The present study will enhance the theoretical databases of line shape parameters for the H$_2$O-CO$_2$ and HDO-CO$_2$ systems, calculate D$_2$O-CO$_2$ line shape parameters and create line lists for these molecules in the 1100-4100 cm$^{-1}$ range. The quantum transitions for H$_2^{16}$O, H$_2^{18}$O, H$_2^{17}$O, HD$^{16}$O, HD$^{18}$O, and HD$^{17}$O are from the 2012 HITRAN database and those for D$_2^{16}$O are from the ab initio line list of Shirin et al. The database was constructed using the best available measured parameters, augmented with theoretical calculations. The half-width, $\gamma$, its temperature dependence, $n$, and the line shift, $\delta$, are for CO$_2$ as the colliding partner and for self collisions. The resulting database contains data for 282,557 transitions of the seven isotopologues of water in the 1100 to 4100 wavenumber range. This project is a collaboration between UMass Lowell, the College of William and Mary, NASA Langley Research Center, and the Jet Propulsion Laboratory to aid the upcoming ExoMars Trace Gas Orbiter mission. The final database, incorporating HDO measurements, will be provided to the ExoMars team.

HIGH RESOLUTION INFRARED SPECTROSCOPY OF ASTROPHYSICALLY RELEVANT MOLECULAR CATIONS

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Many molecular cations are considered to play a key role in the gas-phase chemistry network of the interstellar medium (ISM), in particular in the formation pathways of larger organic species like unsaturated hydrocarbon chains and polycyclic aromatic hydrocarbons (PAHs). Some of the interstellar cations, e.g., HO$_2^+$ and C$_6$H$_7^+$, are also expected to be tracers for the presence of centrosymmetric molecules in the ISM that are not accessible by radio astronomy. However, the lack of accurate spectroscopic data measured from laboratory experiment prohibits a direct astronomical search for most of these important cations in space. In the Sackler Laboratory for Astrophysics, Leiden Observatory, we have recently developed a new instrument, the Supersonic Plasma InfraRed Absorption Spectrometer (SPIRAS), which employs ultra-sensitive and highly precise IR continuous wave cavity ring-down spectroscopy (cw-CRDS), combined with supersonic plasma expansions, and is fully devoted to the spectroscopic study of astrophysically relevant molecular ions and radicals. With this setup, we have recently realized the first gas-phase detection of the smallest aromatic molecule, c-C$_3$H$_3^+$. The main deliverables of this experiment are accurate molecular constants and/or line positions that will be used to interpret or guide astronomical observations, both directly in the IR and indirectly in the radio/submm range.

Methyl iodide CH$_3$I plays an important role in the natural iodine cycle and participates in atmospheric ozone destruction. It is produced by the oceans and mainly removed from the atmosphere by solar ultraviolet radiation$^1$. It has been found to be the dominant gaseous organic iodine species in the earth’s lower atmosphere. Then precise knowledge of spectroscopic line parameters, such as line positions, pressure broadening-coefficients and integrated absorption coefficients is useful for the interpretation of high resolution collisional spectra of CH$_3$I in the atmospheres.

In this work we present theoretical calculations of linewidth of CH$_3$I self-perturbed and perturbed by N$_2$ for more than 100 lines in five $Q$ sub-branches at room temperature in the $\nu_5$ perpendicular band centered at 1435.5 cm$^{-1}$. The calculations were performed using a semi classical model based on Robert-Bonamy formalism with a predominantly electrostatic potential due to large permanent multipole moments of CH$_3$I. These calculations lead to larger results than the experimental data using tunable diode laser high-resolution absorption spectroscopy$^2$. By limiting the integration of the interruption function to an impact parameter equal to 30 Ångström, quite satisfactory results have been observed. The overall decrease in the experimental results with increasing $J$ is well reproduced theoretically.

We have examined the dependence of self and N$_2$-broadening coefficients on $J$ and $K$ quantum numbers. The self-broadening coefficient was found to increase with $J$ for $J \leq 25$. This variation presents a maximum around $J = 25$. Whereas the N$_2$-broadening coefficients have a maximum around $J = 15$. The general trend for these coefficients is to decrease with increasing $K$. This decrease is more significant at low $J$ than at high $J$ values.


CONTINUOUS-WAVE LASER AND OPTICAL FREQUENCY COMB CAVITY-ENHANCED SPECTROSCOPY OF CO AT 1.58 µm

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A great potential of cavity-enhanced absorption spectroscopy (CEAS) in application to ultrasensitive spectra measurements comes from significant elongation of optical path inside the high-finesse cavity. Cavity Ringdown Spectroscopy (CRDS) is an established technique based on variation of interaction time of the laser light with the optical cavity. Insensitivity to the laser power fluctuations and negligible influence of instrumental function make it a powerful tool for sensitive trace gas detection or detailed spectral lineshape analysis. Absorption spectroscopy based on optical frequency comb (OFC) allows measurements of molecular absorption spectra in a wide spectral range with high signal-to-noise ratios. It removes the limits of cw-laser spectroscopy caused by usually time-consuming non-continuous tuning and limited operational frequency range. Fourier transform spectrometers (FTS) based on OFCs allow detection of broadband spectra within acquisition times orders of magnitude shorter than traditional FTIRs based on thermal sources 1. The sensitivity can be increased by coupling the OFC light to the optical enhancement cavities 2. Moreover, the resolution of OFC-based FTS is not limited by the maximum optical path difference (OPD) between the interferometer’s arms 3. It makes it suitable for simultaneous acquisition of tens of molecular lines in wide pressure range.

We present CEAS measurements of a band of CO around 1.58 µm, performed both with CRDS and OFC-CEAS setups. The first experimental setup is using frequency stabilized Pound-Drever-Hall locked CRDS spectrometer 4, linked to optical frequency comb referenced to Rb frequency standard. It uses an enhancement cavity of finesse of 13000, reaching the sensitivity of $7 \times 10^{-11}\text{cm}^{-1}$ and absolute frequency accuracy below 100 kHz. The broadband

system is based on Er:fiber femtosecond laser, locked with two-point PDH locking scheme\(^5\) to an enhancement cavity of finesse of 8500. The spectrum is recorded by high-speed FTS using balanced-detection scheme. The results of the measurements of the same gaseous sample obtained with both systems will be presented and compared in detail. It will include the accuracy of mixing ratio determination as well as the accuracy and precision of retrieved absolute line positions and lineshape parameters for several CO lines in the measurement’s range.

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WATER VAPOR CONTINUUM IN THE RANGE OF ROTATIONAL SPECTRUM OF H$_2$O MOLECULE: NEW EXPERIMENTAL DATA AND THEIR COMPARATIVE ANALYSIS

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Water vapor continuum plays an important role in the Earth radiation balance affecting weather and global climate changes. In spite of long considerable experimental and theoretical efforts through all over the world the continuum is still poorly studied and understood. We present new experimental measurements of the water vapor continuum absorption in the range covering the essential part of the pure rotational spectrum of H$_2$O molecule from 15 up to 200 cm$^{-1}$. The continuum absorption was derived from the broad band water vapor spectra recorded at room temperature at Soleil synchrotron employing the 150-m mutipass gas cell supplying the record sensitivity and high quality of experimental data. The new data considerably extend and unify diverging results of previous measurements of the continuum performed in several spots within the range from about 3 up to 90 cm$^{-1}$. The new evidence of significant contribution of the water dimer to the continuum formation is revealed in the range of 15-35 cm$^{-1}$. The continuum spectrum in this range show the characteristic knee very similar to that predicted by the most rigorous to date ab initio calculation of the water dimer absorption. The continuum retrieved in the 40-200 cm$^{-1}$ range revealed that the widely used in atmospheric applications MT-CKD empirical formulation of the continuum gives qualitatively correct frequency dependence but overestimate the continuum amplitude by about 40%. Analysis of the possible cause of the observed continuum reveals that the significant part of the observed continuum in the range of the maximum intensity of water monomer rotational spectrum can not be explained within the current understanding of the continuum origin.
ON THE CALCULATIONS OF THE INFLUENCE OF A COLLISIONAL CORRELATION ON THE DICKE NARROWING OF A SPECTRAL LINE SHAPE

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Molecular line shapes are affected by several physical effects. In addition to well-known Doppler broadening and collisional broadening and shifting, many other effects like both the molecules’ center-of-mass velocity changes, Dicke narrowing, the speed dependence of collisional broadening and shifting or line mixing should be taken into account. In this work we focus on the Dicke narrowing effect for the collisionally broadened and shifted lines.

As it was shown earlier\(^1\) a correlation between the velocity-changing and dephasing collisions can result in a significant reduction of the Dicke narrowing effect. In some cases also an asymmetry of the line shape can be expected. Here, we employ the classical line-shape theory to investigate this effect in more detail. We aim for an analysis of the influence of the velocity-changing and dephasing collisions’ correlation on the shape of spectral lines in a case of atom-molecule systems. Recently, it has been demonstrated that a shape of the interaction potential can affect significantly the calculated line profiles\(^2\). In our calculations classical (empirical) as well as high-level quantum-mechanically \textit{ab initio} evaluated interaction potentials for some model systems are used.

ASSIGNMENTS OF $^{15}$NH$_3$ TRANSITIONS IN THE 2.3 MICRON RANGE

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Ammonia is one of the key molecules observable in extra terrestrial planets and other astronomical objects. The correct assignment of experimentally observed transitions is also vital for benchmarking the theoretical models or the precise retrieval of isotopologues ratio.

The spectra of $^{15}$NH$_3$ were recorded using VECSEL (Vertical External Cavity Surface Emitting Laser) source in the range from 4275 to 4356 cm$^{-1}$ previously described in Čermák et al. The measurements were performed at three temperatures 185 K, 210 K and 296 K for pressures up to 10 mbar in order to properly observe weak transitions. The line positions were compared with Yurchenko’s theoretical model and Urban’s experimental data et al. The derived lower state energy was compared with Yurchenko’s list for the 300 K temperature. The assignment method was based on GSCD (Ground State Combination Difference) with consideration of the lower state energy of the transition, position of the line and the tendency of the line assignment within the band. The assignments were provided for the $\nu_1 + \nu_2$, $\nu_2 + \nu_3$ and $\nu_2 + 2\nu_4$ bands as well as for the $2\nu_2 + \nu_3 - \nu_2$ hot band.

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CALIBRATION-FREE MEASUREMENTS OF ROTATIONAL TEMPERATURE IN ATMOSPHERIC DISCHARGES BY THE \( \text{N}_2 \) HERMAN INFRARED SYSTEM

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Optical Emission Spectroscopy (EOS) is an important method for investigation of discharge radiation with a possibility to determine its properties such as rotational temperature. It is a very important parameter as in many cases it can be used for monitoring the gas temperature\(^1\).

In this work we present an application of a rovibrational model of the emission spectra of the Herman Infrared (HIR) \( \text{N}_2 \) transition \((C^v{^5}\Pi_u \rightarrow A^5\Sigma_g^+)\). Based on our previous work in the UV part of spectra,\(^2\) we have developed a fitting algorithm which allows determining automatically both the rotational temperature and the sensitivity of the detection scheme directly from the recorded discharge HIR spectrum without any need of pre-calibration.

There are couple of reasons for using the HIR transition for monitoring the temperature of discharges (mostly at atmospheric pressure): Currently, the most frequently systems used for this task lie in the UV part of spectra (e.g. NO gamma or the Second Positive system of \( \text{N}_2 \)), however this range is (at least for the moment) out of reach for some new emerging technologies in spectroscopy, such as sCMOS cameras or compact spectrometers based on SWIFT technology\(^3\). Secondly, HIR is an important direct marker of the \( \text{N}_2(A^3\Sigma_u^+) \) population, which is one of the most important metastable states in atmospheric pressure plasma\(^4\). By coupling the PGOPHER\(^5\) simulation tool and the spectroscopic constants obtained from high resolution experiments, we were able to synthesize the HIR spectrum with sufficient quality so that the

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\(^1\)P. J. Bruggeman, N. Sadeghi, D. C. Schram and V. Linss, Plasma Sources Sci. Technol. 23 (2014) 023001
\(^5\)PGOPHER version 8.0, C M Western, 2014, University of Bristol Research Data Repository, doi:10.5523/bris.hufggypcuc1zvlqed497r2
fitting program can separate the contributions from different HIR vibrational bands and the sensitivity function.
GENERALIZED HYPER-RAMSEY RESONANCE WITH SEPARATED OSCILLATING FIELDS

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We have established an accurate formalism to analyze an extended version of the Ramsey interrogation scheme (1) in high-resolution spectroscopy of atomic, molecular and nuclear narrow transitions. It is based on the design, implementation, and interpretation of composite pulse sequences with the Hyper-Ramsey Resonance (2) to upgrade high resolution frequency measurement in optical clocks, in Penning trap mass spectrometry, for a better control of light induced frequency shifts in matter wave interferometer or quantum information processing.

We derive the analytical form of the Generalized Hyper-Ramsey Resonance (3) to improve ultra-high precision measurement and quantum state engineering when a particle is subjected to controllable separated oscillating fields. The phase-shift accumulated at the end of the interrogation scheme and associated to the particle wave-function is offering a very high-level control of quantum states in various laser parameters conditions. Non-linear behaviors of the central fringe frequency-shift versus a small frequency perturbation in the clock detuning have also been investigated and compared to the usual Ramsey probing scheme for a two-level and three-level systems in Yb and Sr optical clocks (4).

Methyl salicylate has been the subject of intense spectroscopic and theoretical studies since the discovery of its dual fluorescence signal in the 1950s by Weller.\textsuperscript{1} To explain his observation, Weller proposed that a double well potential exists in the electronically excited state. Upon excitation, methyl salicylate undergoes an intramolecular proton transfer to reach the second well, from which an additional fluorescence signal originates. Subsequent studies suggested that the proton transfer in the excited state is barrier-less, such that the double well cannot explain the dual fluorescence.\textsuperscript{2} Since then, two different ground state rotamers were made responsible for the dual fluorescence,\textsuperscript{3} although Caminati and co-workers were unable to identify the second rotamer spectroscopically.\textsuperscript{4} Very recently, a promising proposal was made, which relates the dual fluorescence to two different methyl salicylate - solvent conformers in the ground state;\textsuperscript{5} however, only one methyl salicylate - water conformer could be identified in an earlier infrared study.\textsuperscript{6}

We have identified two conformers of the methyl salicylate - water complex using microwave rotational spectroscopy. This finding lends support to the newly proposed mechanism for the dual fluorescence. Tunneling splittings observed in the spectra are interpreted in terms of methyl internal rotation and motions of the water sub-unit. A thorough search for the second rotamer in the ground state of methyl salicylate will be described.

\textsuperscript{1}A. Weller, \textit{Z. Elektrochem.} \textbf{60}, 1144 (1956).
THE INTERPLAY OF INTRA- AND INTERMOLECULAR HYDROGEN BONDS IN PROLINOL AND ITS COMPLEXES WITH WATER

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Beta amino alcohols are found in a large variety of biologically important compounds, such as natural products, synthetic drugs, and a growing number of ligands and chiral auxiliaries for asymmetric synthesis. Their conformational analysis is of interest to improve our understanding of stereocontrol, and a first step to investigate the interactions involved in the molecular recognition and self-assembly processes in which they participate.

We have investigated the amino alcohol prolinol and its complexes with water using a chirped-pulsed Fourier transform microwave spectrometer at University of Virginia1,2. Prolinol had been previously studied by FTIR spectroscopy3, where it was speculated that two conformers contributed to the spectrum. Conclusive identification of two conformers of prolinol has now been achieved through the analysis of its rotational spectrum. The spectra of the $^{13}$C and $^{15}$N isotopologues of both conformers have been observed in natural abundance, which allowed accurate determination of their Kraitchmann ($r_s$) and effective ($r_0$) structures. The two observed conformers of prolinol are stabilised by an O-H···N hydrogen bond, and differ in the puckering of the pyrrolidine ring and the orientation of the –CH$_2$OH group. In addition, four species of the 1:1 complex of prolinol with water have been identified. Water binds to the two conformers of prolinol forming two insertion and two addition structures, where water is inserted into the prolinol O-H···N hydrogen bond or binds to the hydroxyl group of prolinol as a hydrogen donor without disrupting the intramolecular hydrogen bond.

GLYCOLALDEHYDE DIMER: MOLECULAR RECOGNITION OF SIMPLE SUGARS IN THE GAS-PHASE

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Molecular complex formation in nature is often initiated by molecular recognition. Carbohydrate chains on cell surfaces, for example, can strongly contribute to recognition processes by forming hydrogen bonds or weak CH-π interactions. Here we have studied the dimer of glycolaldehyde (C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}), which is formally the smallest sugar molecule, as it contains an aldehyde- and a hydroxy-group. Furthermore, glycolaldehyde was the first and so far the only sugar found in space\textsuperscript{2}

The glycolaldehyde dimer was studied previously by supersonic-jet infrared and Raman spectroscopy\textsuperscript{3}. In a comparison with high-level ab initio calculations, two low energy glycolaldehyde dimer structures were identified, differing in the formation of intra- and intermolecular hydrogen bonds. Here, we extend this study, using high-resolution microwave spectroscopy, to determine the precise structure of glycolaldehyde dimer in the gas phase by isotopic substitution in natural abundance. The presence of the most stable dimer, forming two intermolecular hydrogen bonds, is confirmed. The high sensitivity of our spectrometer allowed us to assign the spectrum of glycolaldehyde dimer and all of its singly \textsuperscript{13}C- and \textsuperscript{18}O-substituted species in natural abundance. A second set of rotational transitions, which shows splitting of the

\textsuperscript{1}The author thanks "The Hamburg Centre for Ultrafast Imaging" for financial support
transitions potentially due to hydrogen tunnelling, might arise from a second dimer structure.
HIGH ACCURACY COMPUTED LINE LISTS FOR $\text{H}_2^{17}\text{O}$ AND $\text{H}_2^{18}\text{O}$

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Hot line lists for two isotopologues of water, $\text{H}_2^{17}\text{O}$ and $\text{H}_2^{18}\text{O}$, are presented. The calculations employ a newly constructed potential energy surface (PES) and which takes advantage of a novel method for using the large set of experimental data for $\text{H}_2^{16}\text{O}$ to give high quality predictions for $\text{H}_2^{17}\text{O}$, $\text{H}_2^{18}\text{O}$. We required a PES which would satisfy two criteria. First, that it should be at least as accurate as the PES used for the BT2$^1$ line list for which the calculated energies up to 30 000 cm$^{-1}$ and, second, the PES should be adapted to the calculation of energy levels of the two water isotopologues $\text{H}_2^{17}\text{O}$ and $\text{H}_2^{18}\text{O}$. The list of known experimental energy levels for both isotopologues is significantly less extensive than for $\text{H}_2^{16}\text{O}$, we therefore decided to fit a Born-Oppenheimer (BO) mass-independent PES to the available experimental data for $\text{H}_2^{16}\text{O}$ and fix BO diagonal correction (BODC), mass-dependent surface to its \textit{ab initio} value. We used the same fitting procedure as $^2$. For the fit we used data for $J = 0, 2, 5$ rotational states from $^3$. Nuclear motion calculations were performed using DVR3D $^4$ and energy levels were calculated for $J$ up to 50 and in the energy range 0 - 30 000 cm$^{-1}$. This procedure for the PES greatly extends the energy range for which PES can be accurately determined, allowing accurate prediction of higher-lying energy levels than are currently known from direct laboratory measurements. The energy levels and wavefunctions for each isotopologue were combined with a high-accuracy, \textit{ab initio} dipole moment surface $^5$ in the computation of all transition frequencies and associated Einstein A coefficients for states with rotational excitation up to $J = 50$ and energies up to 30 000 cm$^{-1}$. These line lists complement the well-used BT2 $\text{H}_2^{16}\text{O}$ line lists.

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We present a complete water line list which includes all the transitions involving energies up to 40 000 cm\(^{-1}\) and \(J\) up to 72. With no available, globally accurate water potential energy surface (PES), we created one using our previous experience in producing very accurate PESes of water \(^1\). For this we used two sets of data on water energy levels. The first set consists of the spectroscopy data up to 25 000 cm\(^{-1}\) and the second set comprises energy levels from 27 000 cm\(^{-1}\) up to dissociation limit. We used a Varandas-type analytic form to represent the potential. The final PES was obtained by fitting to experimental energy levels up to 40 000 cm\(^{-1}\) and rotational excitations up to \(J=5\). We made separate fits for the lower portion and upper portion of the PES, so the final PES has two sets of constants. Extension to rotational quantum numbers \(J\) up to 72 covers all the bound state rotational states. Our PES is the most accurate global water PES ever. For calculating energy levels we used DVR3D and ROTLEV suites. The energy levels together with the corresponding wave functions are used to compute transition dipoles using the program Dipole from the DVR3D program suit\(^2\). These data are used in program Spectra to calculate the centres and intensities of the water transitions in the region from 0 to 40 000 cm\(^{-1}\). For Dipole program was used very accurate \textit{ab initio} LTP2011 dipole moment surface (DMS)\(^3\), which reproduces available high precision experimental intensities with the accuracy of about 1 %. The accuracy of the energy levels is about 0.1 cm\(^{-1}\) for all the energies up to dissociation. For the well-studied region below 25 000 cm\(^{-1}\), the accuracy is significantly better. For room temperature we computed a separate more accurate linelist, based on the previously obtained accurate PESes. The average accuracy of 0.04 cm\(^{-1}\) is characteristic for this reduced line list. The final line list contains 1 116 560 energy levels.

ELECTRONIC ENERGY TRANSFER IN NaK: IDENTIFICATION OF A\(^1\)Σ\(^+\)–X\(^1\)Σ\(^+\) TRANSITIONS IN COLLISIONALLY INDUCED FLUORESCENCE

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Recent analysis of term energies in the A\(^1\)Σ\(^+\)/b\(^3\)Π complex in NaK\(^1\) has given a reliable description of the e parity levels of the A\(^1\)Σ\(^+\)/b\(^3\)Π complex from 11560 to 15500 cm\(^{-1}\). Term energies derived from multiple electronic systems were treated by fitting V(R) for the A\(^1\)Σ\(^+\) and b\(^3\)Π states to analytical potentials,\(^2\) with Morse-type spin-orbit functions describing the coupling between them. This ‘DVR’ approach has the great advantage of interpolating and extrapolating much more reliably to unobserved \(v, J\) levels than traditional parameter fits. Rotational and vibrational relaxation made significant contributions to data recorded for the A-X system in that work: the experimental conditions (heatpipe source operating around 380 K, in the presence of 2-5 torr Argon) facilitate \(J\)- and \(v\)-changing collisions. When the experiment was operated with Rhodamine dye to excite the higher-lying B\(^1\)Π state, we found that the obvious features of the fluorescence spectrum, rotationally relaxed B\(^1\)Π → X\(^1\)Σ\(^+\) progressions, were sometimes accompanied by dense bands around 10000 cm\(^{-1}\). No patterns were obvious in this region (see figure).

Now that the A\(^1\)Σ\(^+\)/b\(^3\)Π complex is understood, we have at last been able to identify the strongest features of this system as A\(^1\)Σ\(^+\)–X\(^1\)Σ\(^+\) emission, apparently following complete scrambling of rotational quantum number \(J\). A preliminary analysis will be presented.\(^3\)

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\(^1\)Harker et al, Phys. Rev. A. 00 002500 (2015, in press)
\(^3\)We are grateful to the CNRS program PICS for financial support that made this collaboration possible.
H-BOND TOPOLOGY IN THE TRIFLUOROETHANOL TRIMER

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Trifluoroethanol (TFE) is widely used as a co-solvent for studies of the secondary and tertiary substructures of polypeptides and proteins in aqueous solution. TFE and its related family members are also known to promote chirality induction and amplification processes. While the detailed mechanisms for these events are still sketchy, small fluoroalcohol aggregates were proposed to be a key factor in the protein structural altering process. Our group recently reported a rotational spectroscopic study of the TFE dimer where strong preference for the homochiral species was identified. In the current study, we apply chirped-pulsed and cavity-based Fourier transform microwave spectroscopy, complemented with ab initio calculations, to investigate how the H-bond topology changes going from the TFE dimer to the TFE trimer. Special attention was paid to the conformation of the TFE building blocks and the H-bonds involving organic flourines in the trimer. We further highlight the different binding topologies among trimers of TFE, 2-fluoroethanol, and phenol, and emphasize the role of chirality in the stability of these fluoroalcohol aggregates.

SPECTROSCOPIC IDENTIFICATION OF
α,α-DICHLOROBENZYL RADICAL FROM CORONA
DISCHARGE OF BENZOTRICHLORIDE

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Over the past twenty years, we have observed vibronic emission spectra of ring-substituted benzyl radicals, so called benzyl-type radicals, by employing a technique of corona excited supersonic jet expansion to generate the transient species which are believed to play a crucial role in chemical reaction as reaction intermediates. From the analysis of the spectra observed, we could identify the electronic transition energies and vibrational mode frequencies of difluoro-, dimethyl-, and dichloro-substituted benzyl radicals. Very recently, we produced the vibronic excited but jet-cooled α,α-dichlorobenzyl radical from corona discharge of benzotrichloride precursor seeded in a large amount of carrier helium using a pinhole-type glass nozzle developed in this laboratory, from which the visible vibronic emission spectrum was recorded using a long path double monochromator. From an analysis of the spectrum observed, the electronic energy of the D_1 → D_0 transition and a few vibrational mode frequencies in the ground electronic state were obtained for the α,α-dichlorobenzyl radical by comparing the observed frequencies with those of an ab initio calculation. In this presentation, we will discuss the details of the scheme for the production of the radical species and the assignments of vibronic bands from the spectra as well as the substituent effect on the electronic transition energies. The substituent effect is recently rationalized to describe the interaction of benzene ring and substituents on the benzene ring.
FOURIER TRANSFORM $^{12}\text{CH}_3\text{D}$ SPECTRA IN THE REGION 3800 – 8000 cm$^{-1}$. DIRECT COMPARISON TO AB INITIO CALCULATION

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The spectra of $^{12}\text{CH}_3\text{D}$ isotopologue has been recorded in the all region 3800 - 8000 cm$^{-1}$ using the Step-by-Step Fourier Transform spectrometer of G.S.M.A. at Reims university. The region was studied using four optical filters with maximum optical path differences of 0.7 and 1 meter. The Fourier Transform Spectrometer was fitted with a tungsten light source. The light power was limited at the entrance of the spectrometer using a 5 mm-diameter iris. The detection was performed using a pair of InSb detectors.$^1$ The $^{12}\text{CH}_3\text{D}$ gaz has been purchased at EURISO-TOP with an isotopic purity of 98 %. It was used to fill our 2 meter base long White-type cell built in the frame of a previous french ANR support for methane studies. Two absorption paths of 8 and 40 meters were used with the same amount of gaz corresponding to a pressure of 1.7 torr.

The spectra obtained show an important number of structures belonging to several polyads of $^{12}\text{CH}_3\text{D}$ and the determination of lines parameters will be made further. This poster presents the first comparison to the $ab\ initio$ calculations of Rey et al.$^2$ The theoretical calculations of the involved teams already brought decisive information for the analysis of the main isotopologue$^3$ spectra and will now serve the analysis of $^{12}\text{CH}_3\text{D}$.


$^2$ M. Rey, A. V. Nikitin and Vl. G. Tyuterev: Accurate first-principles calculations for $^{12}\text{CH}_3\text{D}$ infrared spectra from isotopic and symmetry transformations. J. C. P. 141, 044316 (2014).

This work is partly supported by French-Russian LIA SAMIA and Tomsk State University Mendeleev grant program.
PRESENT STATUS AND PERSPECTIVES OF LINE-BY-LINE ANALYSES OF THE PH$_3$ ABSORPTION SPECTRUM IN THE OCTAD RANGE BETWEEN 2800 AND 3600 cm$^{-1}$

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A new study of PH$_3$ line positions and intensities was performed for the lower portion of the Octad region between 2800 and 3600 cm$^{-1}$ using high resolution Fourier transform spectra. Line positions and intensities were retrieved by least square curve-fitting procedures and analyzed using the ab initio based effective Hamiltonian and the effective Dipole moment expressed in terms of irreducible tensor operators adapted to spherical top molecules. A new measured line list produced positions and intensities for more 7200 features. Assignments were made for 60 procents of these; 4500 experimental line positions and 1300 selected line intensities were fitted with RMS standard deviations of 0.006 cm$^{-1}$ and 15 procents, respectively. The sum of calculated intensities between 2700 and 3650 cm$^{-1}$ is in a good agreement with HITRAN2012 and is 5-13% lower than sum of calculated intensities from different ab initio dipole moment surfaces. The integrated intensities of lower polyads was calculated.

This work is supported by French-Russian LIA SAMIA. A. V. NIKITIN and Y. A. IVANOVA thanks the Tomsk State University and Academic D.I. Mendeleev Fund Program. Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, NASA Langley Research Center, and Connecticut College, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

HIGH-PRECISION CAVITY RING-DOWN SPECTROSCOPY OF THE MOLECULAR OXYGEN $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ BAND

J. T. HODGES, V. T. SIRONNEAU, A. J. FLEISHER, D. A. LONG, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, U.S.A

We perform optical frequency comb (OFC) referenced frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) of the molecular oxygen $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band at pressures ranging from 0.1-133 kPa in order to gain high-precision data on line intensities, shapes, mixing, and background collision induced absorption (CIA). These measurements with a relative precision of $\approx 0.2\%$ will provide improved reference data for field and satellite-based atmospheric chemistry campaigns such as TCCON, OCO-2 and GOSAT.

At low pressure ($< 10$ kPa) we observe a surprising trend in the measured line intensities. In pure $O_2$, there is an apparent increase in individual line intensities as pressure decreases, suggesting a competition between collisional deactivation of the excited state and other collision-dependent processes such as CIA. This trend was not observed in the spectra of other molecules, specifically in the FS-CRDS of $H_2O$ performed using the same spectrometer and with similar 0.2% relative precision\(^1\). Further investigations with non-$O_2$ collisional partners He, $N_2$, and $SF_6$ reveal significantly different trends in apparent line intensity versus pressure. A model of these observations involving CIA between the three metastable electronic states of $O_2$ will be presented.

We acknowledge financial support from the NIST Greenhouse Gas Measurements and Climate Research Program.

Invited Lectures I

Wednesday, August 26, 9:00

Chair : M. ROTGER
ENANTIOMER DIFFERENTIATION USING BROADBAND ROTATIONAL SPECTROSCOPY (45 min.)

MELANIE SCHNELL, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

Most molecules of biochemical relevance are chiral. Even though the physical properties of two enantiomers are nearly identical, they can exhibit completely different biochemical effects, such as different odor in the case of carvone. In nature and as products of chemical syntheses, chiral molecules often exist in mixtures with other chiral molecules. The analysis of these complex mixtures to identify the molecular components, to determine which enantiomers are present, and to measure the enantiomeric excesses (ee) remains a challenging task for analytical chemistry.

We recently experimentally demonstrated a new method of differentiating enantiomeric pairs of chiral molecules in the gas phase. It is based on broadband rotational spectroscopy and is a three-wave mixing process that involves a closed cycle of three rotational transitions. The phase of the acquired signal bares the signature of the enantiomer, as it depends upon the product of the transition dipole moments, and the signal amplitude is proportional to the ee. A unique advantage of our technique is that it can also be applied to mixtures of chiral molecules, even when the molecules are very similar.

In my lecture, I will introduce the technique and give an update on the recent developments.
PROBING DYNAMICS VIA HIGH RESOLUTION INFRARED SPECTROSCOPY: FROM INTERSTELLAR HYDROCARBON RADICALS TO COLLISIONS AT GAS-LIQUID INTERFACES

(45 min.)

D. J. NESBITT, JILA, National Institute of Standards and Technology and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado Boulder, CO 80309

This talk will address two areas of recent research interest in our group focusing on quite different but intimately connected applications of high resolution laser spectroscopy to molecular dynamics. 1) The first area is based on sub-Doppler infrared absorption spectroscopy (0.001 cm$^{-1}$) in slit supersonic expansion discharges, which provides a remarkably versatile and yet sensitive probe for study of “hot” (i.e., highly reactive) transient hydrocarbon radicals at “cold” interstellar temperatures (10K). By way of example, we will highlight recent spectroscopic results for hydroxymethyl radical (CH$_2$OH), which is thought to be an abundant species in both combustion and the interstellar medium and which exhibits internal rotor tunneling dynamics accessible only with sub-Doppler high resolution methods and jet cooled conditions. 2) The second area involves molecular and quantum state level exploration of collision dynamics at the gas-liquid interface, which we study by generating supersonic beams of jet cooled molecules, bouncing them off freshly formed liquid surfaces in high vacuum, and probing the recoiling molecules with high resolution infrared spectroscopy. Such data, for example, allow us to identify microscopic branching into two distinct channels: “trapping-desorption” events (where molecules “stic” long enough to lose their memory) and “impulsive scatterin” events (where molecules leave within a few collisional interactions). In each area, the overarching goal will be toward comparison between experiment and theory, as well as developing simple physical pictures with which to capture the fundamental chemical physics phenomena.
Invited Lectures J

Wednesday, August 26, 11:00

Chair : D. BERMEJO
Aqueous carbonic acid ($\text{H}_2\text{CO}_3$) is the centerpiece of both the global carbon cycle and physiological buffer systems, yet it remains poorly characterized despite enormous effort. This reflects the fact that carbonic acid is intrinsically unstable upon contact with even a single water molecule, reacting in via a proton chain mechanism to ultimately form aqueous bicarbonate and carbonate anions and hydrated protons, which comprises the reversible mechanism of dissolution of CO$_2$ gas. While solid and gaseous carbonic acid have been studied in some detail, only two spectroscopic studies of the aqueous form have been successful. We report the detection and characterization of both aqueous $\text{H}_2\text{CO}_3$\textsuperscript{1} and dissolved CO$_2$\textsuperscript{2} by X-ray absorption spectroscopy in a liquid microjet designed to effect rapid mixing of reactant solutions, wherein protonation of a bicarbonate solution continuously generates the short-lived acid under ambient conditions. Accompanying first principles calculations of the carbon K-edge transitions facilitate spectral assignment and interpretation\textsuperscript{3}.


LINE SHAPE PARAMETERS FOR MOLECULES OBSERVED IN PLANETARY ATMOSPHERES (45 min.)

R. GAMACHE, Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, 1 University Avenue, Lowell, MA, 01854, USA

The talk focuses on the calculation of line shape parameters for molecules of interest in planetary atmospheres. Due to the typical size and complexity of these molecules, the calculations must employ semi-classical methods. In our lab we used the complex implementation of the Robert-Bonamy (CRB) formalism with a number of improvements. The effects of the trajectory model, complex terms, proper velocity averaging, number of terms in the intermolecular potential, and wavefunctions are discussed and the importance of various terms elucidated. The dependence of the parameters on rotational and vibrational states and on temperature are discussed. Examples will be shown for a number of collision systems such as: H$_2$O-N$_2$, H$_2$O-O$_2$, H$_2$O-Ar, O$_3$-N$_2$, CH$_4$-N$_2$, CO$_2$-N$_2$, CO$_2$-CO$_2$.

The discussion will then move to the more accurate line shape models needed to interpret high-resolution spectra. Several studies on pure water and the water-N$_2$ systems using the Keilson-Storer model, which accounts for collision induced velocity changes and the speed dependence of the collisional parameters, will be shown. Finally, the isolated-line profile for representing high-resolution spectroscopic transitions recommended by an IUPAC Task Group will be presented.


Invited Lectures K,
Mini-Symposium, Excitons, interatomic Coulomb decay, and dipole-dipole interactions
Thursday, August 27, 9:00
Chair : F. MERKT
ICD AND ITS EXPLORATION BY SHORT, INTENSE AND COHERENT LIGHT PULSES (30 min.)

LORENZ S. CEDERBAUM, Department of Theoretical Chemistry
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How does a microscopic system like an atom or a small molecule get rid of the excess electronic energy it has acquired, for instance, by absorbing a photon? If this microscopic system is isolated, the issue has been much investigated and the answer to this question is more or less well known. But what happens if our system has neighbors as is usually the case in nature or in the laboratory? In a human society, if our stress is large, we would like to pass it over to our neighbors. Indeed, this is in brief what happens also to the sufficiently excited microscopic system. A new mechanism of energy transfer has been theoretically predicted and verified in several exciting experiments. This mechanism seems to prevail “everywhere” from the extreme quantum system of the He dimer to water and even to quantum dots. The transfer is ultrafast and typically dominates other relaxation pathways.

To exploit the high intensity of laser radiation available today, we also propose to select frequencies at which single-photon absorption is of too low energy and two or more photons are needed to produce states of an atom that can undergo interatomic Coulombic decay (ICD) with its neighbors. The study can provide a hint how the energy deposited by a FEL on one site in a medium can be transferred fast to the surrounding.

Work on ICD can be found on the ICD Bibliography:
http://www.pci.uni-heidelberg.de/tc/usr/icd/ICD.refbase.html
STATE RESOLVED UV STUDIES OF FLEXIBLE BICHROMOPHORES (30 min.)

DAVID F. PLUSQUELLIC\textsuperscript{a}, TIMOTHY S. ZWIER\textsuperscript{b}, \textsuperscript{a}Physical Measurement Laboratory, National Institute of Standards and Technology, Boulder, CO 80305, \textsuperscript{b}Department of Chemistry, Purdue University, West Lafayette, IN 47907

The flexible bichromophores, diphenylmethane and its analogs, have served as prototypical molecules for investigating the excitonic coupling between identical chromophores since the 1950s. The close proximity of the two benzyl moieties and the flexible linkages between them have resulted in a wide range of transition dipole moment (TDM) orientations and inter-chromophore coupling strengths with splitting between the $S_1/S_2$ electronic states ranging from $<1$ cm$^{-1}$ to more than 100 cm$^{-1}$. We report the state resolved studies for a series of bichromophores\textsuperscript{1,2,3} using several techniques in jet-cooled environments and discuss the rotational structure and perturbations, the TDM orientations and models, the internal mixing and vibronic coupling interactions observed for several of these systems.

Atoms in Rydberg states of high principal quantum number $n$ exhibit unusual physical properties such as large size, long lifetime, and high polarizability, leading to strong interatomic interactions. These strong and long-ranging interactions are the basis for many applications of Rydberg atoms, e.g., for the excitation-blockade effect in quantum optics experiments\(^1\). High-resolution spectroscopy of ultracold samples, in our case atomic cesium, allows us to investigate these interactions in detail and improve our understanding of the relevant couplings.

In a first part I shall discuss interactions leading to the formation of Cs$_2$ dimers in which both atoms are excited to high Rydberg states. These dimers are commonly referred to as macrodimers and are observed in our experiments following Rydberg excitation with an intense, pulsed UV laser. The interactions between the two Rydberg atoms giving rise to these macrodimers are modeled using a long-range multipole expansion, with relevant contributions from terms up to octupole-octupole interactions\(^2\).

In a second part I shall discuss molecules, in which one of the atoms is in a high Rydberg state and is bound to a ground-state atom located inside the orbit of the Rydberg electron. The binding mechanism does not fit into one of the known categories of bonds (covalent, ionic, metallic, or van der Waals) but results from the scattering of the slow Rydberg electron off the ground-state atom\(^3\). Among the unusual properties of these molecules are huge bond lengths exceeding 1000 Bohr radii at $n=30$ and extremely low binding energies (typically much less than 1 GHz)\(^4\). These molecules nevertheless have sharp vibronic levels and high-resolution spectroscopy reveals all details of their structure and dynamics.


Poster Session L
Thursday, August 27, 11:00
ADDITION TO THE HITRAN DATABASE OF LINE-SHAPE PARAMETERS DUE TO THE PRESSURE OF H$_2$, HE and CO$_2$.  
PART 1: SO$_2$, NH$_3$, HF, HCl, OCS and C$_2$H$_2$

J. S. WILZEWSKI$^{a,b}$, I. E. GORDON$^a$, R. V. KOCHANOV$^{a,c}$, C. HILL$^{a,d}$, L. S. ROTHMAN$^a$

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The goal of this work is to increase the potential of the HITRAN database [1] towards the interpretation and modeling of the spectra of atmospheres dominated by noble gases (gas giants) or carbon dioxide (planets like Venus and Mars). Line-broadening coefficients, line shifts and temperature dependence exponents for molecules of planetary interest perturbed by H$_2$, He and CO$_2$ are being assembled from both experimental and theoretical studies, and their extrapolations. The first step in this direction was made by us in Li et al. [2] where we created complete datasets of H$_2$- and CO$_2$-broadened lines of CO. In this work we have extended this study to six more molecules: SO$_2$, NH$_3$, HF, HCl, OCS and C$_2$H$_2$. Semi-empirical approaches used in this work will be described for each system. Every line for these molecules now has the relevant parameters with their uncertainties and source information, which will be accessible through HITRANonline (www.HITRAN.org).

The present work helps to identify the need for further investigations of broadening, shifting and the temperature dependence of spectral lines in planetary environments. A “wishlist” for additional studies in this area will be presented at the meeting.

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References
EXPERIMENTAL AND THEORETICAL STUDY OF N₂-PRESSURE-INDUCED LINE-SHAPE PARAMETERS IN THE \( \nu_3 \) AND \( \nu_5 \) BANDS OF CH₃D

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Methane and its isotopologues play an important role in the terrestrial and planetary atmospheres. The concentration of CH₄ is increasing in the Earth's atmosphere at a rate of about 1% per year and, as an IR-active gas, it contributes significantly to the enhanced greenhouse effect. Methane is also a key constituent of the atmosphere of Titan and other planetary bodies. CH₃D and CH₄ IR features are frequently used for determination of atmospheric H/D ratios. As a consequence, the spectroscopic parameters of CH₃D are continually investigated in order to improve their quality and increase the number of parameters available for remote sensing interpretations.

The present work is focused on an extensive study of the IR absorption of the monodeuterated methane in the parallel \( \nu_3 \) and perpendicular \( \nu_5 \) bands in a temperature range of atmospheric interest (80-300K) with the goal to provide the nitrogen-induced line-broadening and shifting coefficients as well as their temperature dependences for spectroscopic databases. This work continues our previous study of CH₃D-N₂ line-shape parameters in the \( \nu_6 \) band [1].

A set of 23 high-resolution and high signal-to-noise-ratio spectra recorded with two Fourier-transform spectrometers: a) the McMath-Pierce FTS located on Kitt Peak and b) a Bruker IFS 125 HR FTS at the Jet Propulsion Laboratory (JPL) [2] were fit simultaneously in a multispectrum approach [3]. The set included both pure CH₃D and dilute mixtures of CH₃D in research grade nitrogen. Variations in the measured line parameters with the symmetry species, the rotational quantum numbers and with temperature were obtained and compared with previous measurements available in the literature.

The nitrogen-broadening coefficients and the associated temperature-dependence exponents were also evaluated by a semi-classical approach [4] based
on a rigorous treatment of the active molecule as a symmetric top, a model intermolecular potential including both short- and long-range interactions, and exact classical trajectories governed by the isotropic potential. These calculations were done for various temperatures, allowing extraction of the temperature-dependence exponents, and for wide ranges of rotational quantum numbers. These theoretical values compare favorably with our measurements for the experimentally observed $J$ and $K \leq 7$.

CRDS ABSORPTION SPECTRUM OF NATURAL WATER VAPOUR BETWEEN 7911 AND 8337 CM$^{-1}$

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The room temperature absorption spectra of water vapour in natural isotopic abundance have been recorded at two different pressures by Cavity Ring Down Spectroscopy (CRDS) between 7911 and 8337 cm$^{-1}$. The high sensitivity of the recordings ($\alpha_{\text{min}} \sim 2 \times 10^{-11}$ cm$^{-1}$) allows measuring lines with intensities spanning seven orders of magnitude ($3 \times 10^{-30} - 2 \times 10^{-23}$ cm/molecule at room temperature). The experimental line list includes more than 4660 lines. About 1350 lines were assigned to impurities (oxygen, carbon dioxide and ammonia). More than 3190 lines were assigned to 3560 transitions of five water isotopologues ($\text{H}_2^{16}\text{O}$, $\text{H}_2^{18}\text{O}$, $\text{H}_2^{17}\text{O}$, $\text{HD}^{16}\text{O}$, and $\text{HD}^{18}\text{O}$). 126 weak lines left unassigned.

The assignments of water lines were performed using known experimental energy levels as well as calculated line lists based on the results of Partridge and Schwenke. Transitions of 51 rotation-vibration bands with maximum values of rotational numbers $J = 20$ and $K_a = 11$ were determined for the first time. In addition, 43 levels of main isotopologue were found to deviate importantly from those recommended by the IUPAC task group.

Detailed comparisons with the line list of the HITRAN-2012 database illustrate the advantages of the new data set.

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CRDS ABSORPTION SPECTRUM OF $^{17}$O WATER VAPOUR BETWEEN 5850 AND 6670 CM$^{-1}$

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The room temperature absorption spectra of $^{17}$O enriched water vapour at two different pressures (1 and 12 Torr) have been recorded by Cavity Ring Down Spectroscopy (CRDS) spectrometer between 5850 and 6670 cm$^{-1}$. The high sensitivity of the recordings ($\alpha_{\text{min}} \sim 5 \times 10^{-11}$ cm$^{-1}$) allows detecting lines with intensity spanning six orders of magnitude (1.4 x 10$^{-30}$ – 3.6 x 10$^{-24}$ cm/molecule at room temperature). The experimental line list includes more than 10 300 lines. More than 1250 lines of different isotopologues of CO$_2$, OCS, CH$_4$ and HCN, present as impurities were identified and removed from the list.

The assignments of water lines were performed using known experimental energy levels as well as calculated line lists based on the results of Partridge and Schwenke$^1$. More than 8500 lines were assigned to 9630 transitions of six water isotopologues (H$_2$O, H$_2^{17}$O, H$_2^{18}$O, HD$_2^{16}$O, HD$_2^{17}$O, and HD$_2^{18}$O). All transitions of the H$_2$O, H$_2^{18}$O, HD$_2^{16}$O, and HD$_2^{18}$O isotopologues were assigned using experimental energy levels$^2$, $^3$, $^4$, $^5$, $^6$. More than half of the assigned H$_2^{17}$O and HD$_2^{17}$O transitions correspond to new or corrected upper energy levels compared to those reported in Refs. [2-4]. About 1000 new H$_2^{17}$O transitions associate with upper states of the second triad and the first hexad were identified. Main part of the newly assigned HD$_2^{17}$O transitions belongs to the $v_1 + v_3$ and $2v_2 + v_3$ bands. Comparisons of obtained sets of the H$_2^{17}$O and HD$_2^{17}$O energy levels with previously reported results$^2$, $^3$, $^4$, $^7$ are discussed.

$^1$http://spectra.iao.ru/1314x672/ru/mol/survey/1/
MILLIMETERWAVE SPECTROSCOPY OF ETHANIMINE AND PROPA NIMINE AND THEIR SEARCH IN ORION

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The aldimines are important to understand amino acids formation process as they appear in reaction scheme of Strecker-type synthesis. Following the detection in the ISM of methanimine (CH$_2$NH) in 1973$^1$ and the more recent one of ethanimine (CH$_3$CHNH)$_2$, we decided to investigate the next molecule in the series: propanimine (CH$_3$CH$_2$CHNH). For this molecule no spectroscopic information was available up to now. We measured the rotational spectrum of propanimine in the frequency range up to 500 GHz. Since the spectroscopic studies of ethanimine were limited to 130 GHz$^3$, we also extended the measurements up to 300 GHz. The spectra of both E- and Z- isomers are analyzed for the two molecules. Usually aldimines which are unstable molecules are obtained by discharge or pyrolysis methods, here pure sample were obtained by synthesis process. For ethanimine, the methyl top internal rotation should be taken into account, therefore the analysis is performed using new version of RAM36 code$^4$ which includes the treatment of the nuclear quadrupole hyperfine structure. The spectroscopic results and their searches in Orion will be presented. This work was supported by the CNES and the Action sur Projets de l’INSU, PCMI. This work was also done under ANR-13-BS05-0008-02 IMOLABS


FIRST SPECTROSCOPIC STUDIES AND DETECTION IN SgrB2 OF $^{13}$C-DOUBLY SUBSTITUTED ETHYL CYANIDE

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Ethyl cyanide (CH$_3$CH$_2$CN) is one of the most abundant complex organic molecules in the interstellar medium firstly detected in OMC-1 and Sgr B2 in 1977$^1$. The vibrationally excited states are enough populated under ISM conditions and could be detected$^2,3$. Apart from the deuterated ones, all mono-substituted isotopologues of ethyl cyanide ($^{13}$C$^4$ and $^{15}$N$^5$) have been detected in the ISM. The detection of isotopologues in the ISM is important: it can give information about the formation process of complex organic molecules, and it is essential to clean the ISM spectra from the lines of known molecules in order to detect new ones. The $^{12}$C/$^{13}$C ratio found in SgrB2: 20-30 suggests that the doubly $^{13}$C could be present in the spectral line survey recently obtained with ALMA (EMoCA)$^6$, but no spectroscopic studies exist up to now. We measured and analyzed the spectra of the $^{13}$C-doubly-substitued species up to 1 THz with the Lille solid-state based spectrometer. The spectroscopic results and the detection of the doubly $^{13}$C species in SgrB2 will be presented.

This work was supported by the CNES and the Action sur Projets de l’INSU, PCMI. This work was also done under ANR-13-BS05-0008-02 IMOLABS. Support by the Deutsche Forschungsgemeinschaft via SFB 956, project B3 is acknowledged

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2A. Belloche, et al., A&A 2013, 559, A47  
3A.M. Daly, et al., Astrophys. J. 2013, 768, 81  
6Belloche et al. 2014, Science, 345, 1584
SYNCHROTRON-BASED HIGH RESOLUTION THz SPECTROSCOPY BETWEEN 0.8 AND 3 THz USING A COLLISIONAL COOLING MULTIREFLECTION CELL

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One of the great challenges of modern high resolution spectroscopy is to find devices which cover the THz gap between 0.7 and 5 THz. We have extended our high resolution FTIR setup at the Swiss Light Source described in Ref.1,2,3,4,5,6,7 with a collisional cooling multireflection cell which makes it possible to record spectra down to 850 GHz (28 cm\(^{-1}\)). Due to the high brightness of the synchrotron radiation the signal-to-noise ratio is effectively 20 to 50 times better than that of conventional thermal sources in the spectral region below 4 THz. Our resolution is in the order of 17 MHz which makes it possible to measure rotational spectra. Using the collisional cooling method we are able to measure rotationally resolved spectra as low as 80 K or even 10 K. We present an analysis of the rotational spectra of deuterated methanes (CH\(_3\)D, CH\(_2\)D\(_2\), CHD\(_3\)) measured at 80 K in the range 0.7 to 3 THz and the symmetric top molecules CHF\(_3\) and NF\(_3\) measured at 125 K and 110 K, respectively.

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2 S. Albert, K. Keppler, Ph. Lerch, M. Quack, A. Wokaun, J. Mol. Spectrosc. 2015, in press.
METHYL INTERNAL ROTATION IN THE MICROWAVE SPECTRUM OF VINYL ACETATE

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The microwave spectroscopic investigations on allyl acetate, CH$_3$(CO)OCH$_2$C-H=CH$_2$, have shown that the barrier to internal rotation of the acetyl methyl group is 98.093(12) cm$^{-1}$, almost the same as that found for a series of alkyl acetates. Starting from the barriers of 102.413(20) cm$^{-1}$ and 101.606(23) cm$^{-1}$ in methyl acetate and ethyl acetate, respectively, a barrier of approximately 100 cm$^{-1}$ was always found when the alkyl chain is longer, like in the case of n-propyl acetate up to n-hexyl acetate. Even when the alkyl chain is branched like in isopropyl acetate and isoamyl acetate, the internal rotation barrier of the acetyl methyl group seems to be unaffected.

The rotational spectrum of vinyl acetate, CH$_3$(CO)OCH=CH$_2$, where the double bond is attached directly to the carboxyl group and π-electron conjugation becomes possible, were recorded using two molecular beam Fourier transform microwave spectrometers operating in the frequency range from 2 to 40 GHz. Large splittings up to 2 GHz occurred due to the internal rotation of the acetyl methyl group CH$_3$CO with a V$_3$ potential of 151.492(34) cm$^{-1}$, much larger than the 100 cm$^{-1}$ barrier of approximately mentioned above. The torsional transitions were fitted using three different programs, XIAM, ERHAM, and BELGI-Cs, whereby the rotational constants, centrifugal distortion constants, and the internal rotation parameters could be determined with very high accuracy. The experimental results were supported by quantum chemical calculations. For a conformational analysis, potential energy surfaces were calculated.
JET-COOLED BIS(XYLENE)CHROMIUM ROTATIONAL ISOMERS STUDIED WITH HIGH-RESOLUTION LASER IONIZATION SPECTROSCOPY

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The high resolution ZEKE\(^1\) and MATI\(^2\) spectra of substituted bisarene complexes of the Group 6 transition metals appeared to reveal signals corresponding to individual rotational isomers. These data provide an unprecedented accuracy in experimental measuring ionization energies of the sandwich rotamers and vibrational frequencies of the gas-phase sandwich cations. New results on the MATI structures observed for bis(xylene)chromium compounds are presented in this work. The MATI peaks were interpreted on the basis of DFT calculations. The geometries of the ground-state neutral derivatives of o-, m- and p-xylene as well as those of the corresponding ions were optimized at the BPW91/TZVP level of theory. Similar to the toluene complex\(^3\), DFT reveals stable bis(xylene)chromium conformers with eclipsed carbocycles. The calculated ionization energies provide an unambiguous interpretation of the MATI origins observed for each compound. Three rotational isomers were detected for the o-xylene and m-xylene complexes. In the spectrum of bis(p-xylene)chromium two intense peaks correspond to the adiabatic ionization potentials of the isomers with eclipsed and staggered positions of the methyl groups. The ionization energy of each rotamer has been determined experimentally in this work with a 5-cm\(^{-1}\) accuracy. The syntheses of the bis(xylene)chromium complexes and DFT calculations were carried out within the frames of the Project No 14-13-00832 supported by the Russian Science Foundation.

CLS SYNCHROTRON IR AND FIR SPECTROSCOPY OF CD$_3$OH: $\tau$-LADDERS AND VIBRATIONAL DRAINS IN THE METHANOL TORSIONAL BATH

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Structure from high torsional levels and the lower vibrational modes of the CD$_3$OH isotopologue of methanol has been analyzed in Fourier transform spectra recorded at the Far-Infrared beamline of the Canadian Light Source synchrotron in Saskatoon. Torsional assignments in the ground state have been substantially extended from earlier work $^1$$^2$. Energy term values for A and E torsional species of the third excited torsional state, $v_t = 3$, are now almost complete up to $K = 15$, and numerous sub-states have been identified for $v_t = 4$. Analyses of the in-plane CD$_3$ rock, the CO stretch, the symmetric CD$_3$ deformation, the OH bend and the CD$_3$ stretch vibrational modes are also in various degrees of completion. The torsional spectra show interesting close series or "ladders" of strong high-$v_t$ sub-bands related by Dennison’s torsional symmetry index $\tau$, rather than A and E, that can be understood in terms of a simple free-rotor "spectral predictor" chart. The energy curves for the $v_t = 3$ and 4 ground-state torsional levels pass through several of the excited vibrational states, and perturbations to the torsional and vibrational levels reveal numerous near-resonant couplings that can act as doorways or "drains" to channel population between the torsional bath and the vibrational manifold.

IMPLEMENTING PRESSURE BROADENING IN MOLECULAR LINE LISTS FOR APPLICATION TO EXTRASOLAR PLANETS

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ExoMol has previously calculated high resolution temperature dependent cross-sections for selected molecules according to Hill et al. [1]. Pressure dependence is now being implemented for five molecules expected to be of importance in the atmospheres of Hot Jupiter’s, H$_2$O, CO$_2$, CO, CH$_4$ and NH$_3$. Unfortunately there is an overall lack of accurate pressure broadening parameters for high temperature molecular lines and broadening by relevant species, namely H$_2$ and He. For the most part parameters are extrapolated from room temperature and pressure and small quantum numbers or approximated using air with the exception of H$_2$O. For this molecule a data set of H$_2$ and He pressure broadening parameters for molecular lines of importance in the temperature range 500 – 2000 K has been computed by Lavrentieva and Dudaryonok using semi-empirical methods [2, 3].

The pressure-broadened cross-sections are optimised for use in $\tau - RE_x$, an inverse retrieval code for exoplanetary atmospheres [4,5]. $\tau - RE_x$ is a line-by-line radiative transfer fully Bayesian retrieval framework designed with three objectives in mind: (1) Sensitivity: Understanding the limitations and degeneracies of spectroscopic models, (2) Objectivity: Taking into account the widest possible range of atmospheric models and (3) Big Data: Allowing for intelligent automation and scalability to larger computer clusters.

Presented will be a summary of the work done to date including an application to modelling Exoplanet atmospheres using $\tau - RE_x$.

ACCURATE AB INITIO PREDICTIONS OF METHANE SPECTRA UP TO 12000 CM$^{-1}$ AT VARIOUS T-CONDITIONS

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We have recently reported the construction of complete hot methane line lists$^1$ based on accurate *ab initio*$^2,^3$ and variational calculations$^4$ up to 2000 K in the range below 5000 cm$^{-1}$. Here we have extended this work up to 12000 cm$^{-1}$ by gradually decreasing the temperature. Applications for the modeling of the Titan atmosphere in the range 0.8-5µm or of astrophysical objects will be discussed and comparison with available lists (HITRAN$^5$, EXOMOL$^6$) will be given.

This work is supported by French-Russian LIA SAMI and Tomsk State University Mendeleev grant program.

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Difluoromethane (CH$_2$F$_2$, HFC-32) represents an emerging atmospheric pollutant belonging to the family of hydrofluorocarbons (HFCs), and its atmospheric concentration has steadily grown up since 1990s, being around 3 ppt in 2005. This molecule has been proposed as a valid replacement for both chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), in particular HCFC-22, which have been phased out by the Montreal protocol due to their capacity of destroying the stratospheric ozone layer. Nowadays, CH$_2$F$_2$ has commercial applications, in particular it is employed in refrigerant mixtures, together with CF$_3$CH$_3$, CF$_3$CH$_2$F, and CF$_3$CHF$_2$. With respect to analogous CFCs and HCFCs, HFC-32 being chlorine-free does not contribute to the ozone loss, and it has shorter atmospheric lifetime, because it is degraded by reaction with the OH radicals. On the other hand, it represents a greenhouse gas which can contribute to global warming, as the C-F chromophore strongly absorbs the IR radiation around 9 µm.

In the present contribution the room temperature (296 ±1 K) broadening coefficients of CH$_2$F$_2$ either self-broadened or perturbed by N$_2$ and O$_2$ buffer gases have been measured in the 8 µm spectral region by tunable diode laser spectroscopy equipped with a 68.2 cm path length cell. For self-broadening measurements the CH$_2$F$_2$ pressure has been varied between 20 and 800 Pa, while for foreign broadening experiments the radiator pressure has been kept fixed in the interval 99 - 165 Pa (on the basis of the transition intensities) and it has been perturbed by increasing quantities of the damping gases with pressures in the range 200 - 4000 Pa. The recorded transitions belong to the $\nu_7$ band which is located at 1178.7 cm$^{-1}$ and corresponds to the CH$_2$ rocking vibration. The line shape analysis has led to the determination of the self-, N$_2$-, and O$_2$-broadening coefficients for about 50 ro-vibrational transitions with $5 \leq J'' \leq 39$ and $0 \leq K'' \leq 14$.
A VARIATIONALLY COMPUTED LINE-LIST FOR HOT ETHYLENE

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A new theoretical hot line list for ethylene (C$_2$H$_4$) in its ground electronic state for temperatures up to T=2000 K is computed as part of the ExoMol project [1]. Previously constructed semi-empirical potential energy and \textit{ab initio} dipole moment surfaces were used as input for the nuclear motion program ANGMOL [2]. Using ANGMOL we have computed 5 million ro-vibrational energies for 2160 vibrational states and around 200 million transition frequencies, and associated Einstein-A coefficients and absolute transition intensities, at wavenumbers up to 6550 cm$^{-1}$ and rotational excitations up to $J=80$.


The full set of data, in the form of both energies and A coefficients, as well as temperature-dependent cross sections, will be available from the CDS data centre as well as at via www.exomol.com.

Room temperature spectra in the region of the $\nu_{12}$ and $\nu_9$, $\nu_{11}$ bands

This work was supported by the ERC under Advanced Investigator Project 267219.

References

HIGH RESOLUTION INFRARED SPECTRA OF JET-COOLED DI- AND TRI-ACETYLENE

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Polyacetylenes form an important series of unsaturated hydrocarbon compounds that are of astrophysical interest. We present here high-resolution mid-infrared spectroscopic data of diacetylene (HC$_4$H) and triacetylene (HC$_6$H). These are recorded in a supersonically expanding pulsed planar plasma using a narrowband IR-optical parametric oscillator (OPO) based continuous wave cavity ring-down spectroscopy (cw-CRDS). Polyacetylenes are produced by discharging a C$_2$H$_2$/He/Ar gas mixture which is supersonically expanded into a vacuum chamber through a slit discharge nozzle. Experimental spectra of the C-H stretching fundamental bands and also a series of vibrationally hot bands for both HC$_4$H and HC$_6$H are recorded in the 3305-3350 cm$^{-1}$ region. Jet-cooling in our experiment reduces the rotational temperature of both HC$_4$H and HC$_6$H to $\sim$20 K. A detailed rotational analysis on, in total, sixteen bands for HC$_4$H and five bands for HC$_6$H, is performed. Nine for HC$_4$H and four bands for HC$_6$H are reported for the first time. For both molecules improved and new molecular constants of a series of vibrational levels are presented. Combining available data sets, spectroscopic parameters both for the ground state and also all observed excited vibrational states states of the two molecules are accurately determined. Perturbations in the $\nu_5$ (C-H asymmetric stretching) vibrational state of HC$_6$H are also analyzed in detail.$^{1,2}$

AB INITIO STUDY OF THE CH$_4$–Ar POTENTIAL AND INDUCED DIPOLE SURFACES: TRUE BOUND DIMER CONTENT AND COLLISION-INDUCED ABSORPTION

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The role played by methane in various industrial, environmental, atmospheric and astrophysical processes is hard to overestimate. Rigorous characterization of pair intermolecular interaction among CH$_4$ and other species is thus highly demanded from either the theoretical or applicative perspective. Our paper focuses on updating the \textit{ab initio} simulation for the argon–methane potential energy surface (PES), as well as on the first construction of induced dipole surface (IDS) for this system that extends beyond multipolar approximation. Accurate knowledge of both the PES and IDS is required e.g. in order to develop a reliable model for collision-induced absorption (CIA).

First, the PES was generated assuming rigid methane and using CCSD(T) coupled cluster method with aug-cc-pVXZ (X = D, T, Q) basis sets with subsequent extrapolation to the CBS limit. Next, the IDS was calculated with aug-cc-pVTZ basis set augmented with mid-bond wave functions. Both surfaces were then subject to analytical fit in the form of an expansion over spherical harmonics. The quality of the PES was tested through calculation of the mixed second virial coefficient. Classical approach was then used to evaluate equilibrium constant for the formation of true bound CH$_4$–Ar dimers. Finally, our generated PES and IDS were used to trace temperature variations of the CIA rototranslational band spectral moment. The correspondence of the calculated and measured data is discussed. Estimates relevant to the Titan’s atmosphere conditions are given.

This work was partially supported by the RFBR under Grants 13-05-00751 and 15-05-00736.
OXYGEN B-BAND TRANSITIONS FREQUENCIES AND LINE-SHAPE PARAMETERS FOR ATMOSPHERIC APPLICATION

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There is a growing interest in the use of the molecular oxygen B-band for the atmospheric applications including remote sensing for ground-based or satellite measurements. The oxygen spectrum is used mainly for the calibration purposes in simultaneous measurements of greenhouse gases and the atmospheric pressure and temperature profiles determination.

We present the laboratory data for self- and nitrogen-broadened oxygen P- and R-branch of the B-band transitions at around 689 nm. Line shapes were measured at low pressures by the Pound-Drever-Hall-locked frequency-stabilized cavity ring-down spectrometer (PDH-locked FS-CRDS). To assure absolute frequency measurement the spectrometer was equipped with the optical frequency comb (OFC). Data were analyzed by means of several different profiles including the speed-dependent Voigt profile (SDVP). Presented data contain transitions frequencies and line-shape parameters for the transitions with the total angular momentum quantum number for the lower state $J$ reaching up to 21 for P-branch and up to 28 for R-branch. Previously published data \(^1\) are collected and supplemented with data for other transitions. Line positions are compared with HITRAN database and other data available in the literature.


SUBVIBRATIONAL LIF SPECTROSCOPY OF THE $B^31(5^3P_1) \leftarrow X^10^+(5^1S_0)$ TRANSITION IN EXCITATION SPECTRUM OF CdNe VAN DER WAALS COMPLEX

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We present new laser induced fluorescence (LIF) excitation spectra with partially resolved rotational structure and corresponding simulations of two vibrational components of the $B^31(5^3P_1) \leftarrow X^10^+(5^1S_0)$ transition in CdNe complex. The investigated CdNe complexes were produced using a high-temperature pulsed supersonic source of van der Waals diatomic molecules which contain cadmium atom\(^1\). The source was developed in our laboratory. The presented spectra were obtained using an advanced method of selection of optimal time integration window\(^2\). Based on the simulation of the experimental spectra vibrational and rotational molecular constants were estimated. Figure shows an experimental spectrum of the $\nu' = 1 \leftarrow \nu'' = 0$ vibrational component of considered transition (red line) and its simulation (black line) prepared under assumption, that potentials of both states are represented by a Morse function.

The research project is financed by the National Science Centre (Poland) - contract no. UMO-2011/01/B/ST2/00495.
Chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy has proven to be a powerful tool for broadband spectral investigations in the cm-wave band. When used in conjunction with a non-specific production source, such as an electrical discharge or a heated nozzle, large numbers of lines can be quickly observed, but many can not be assigned to known species.

To further investigate these unassigned lines and to identify new molecules, we developed a “spectral taxonomy” approach which leverages the high sensitivity of a traditional cavity FTMW spectrometer. This procedure is composed of three main steps which, thanks to newly-designed control software, can be performed with minimal human intervention:

- A CP-broadband spectrum is recorded and then “cleaned” by removing instrumental artefacts and lines from the precursors and contaminants (e.g. (H₂O)₂);
- Remaining lines are sorted into sub-groups according to their dependance on precursor gas, external magnetic field, discharge, etc.;
- Lines within each taxonomic group are then exhaustively tested with double resonance: these tests link lines which share a quantum state, crucial information that can be used to establish the structure of their carrier.

In this poster, the spectral taxonomy approach will be presented and illustrated by several recent results.
High-resolution absorption spectroscopy in the vacuum ($\lambda < 200\,\text{nm};\,\text{VUV}$) and extreme ($\lambda < 105\,\text{nm};\,\text{XUV}$) ultraviolet ranges of the electromagnetic spectrum is notoriously difficult. VUV radiation from synchrotron sources needs to be monochromatised, which limits the bandwidth of the radiation to at best $0.1\,\text{cm}^{-1}\,1$. VUV-FT absorption spectroscopy, as recently extended to the XUV range offers the multiplex advantage, but so far the best resolution achieved with this method is $0.33\,\text{cm}^{-1}\,2$. Pulsed VUV laser systems based on four-wave mixing enable a higher resolution\,3, but the large pulse-to-pulse fluctuations resulting from the non-linearity of the VUV generation process limits the sensitivity of absorption measurements, so that only very few laser VUV absorption spectra of atoms and molecules in supersonic beams have been reported\,3,4.

To improve the low sensitivity resulting from the large pulse-to-pulse fluctuation of the VUV radiation, Sommavilla et al.\,5 have used a dispersion grating and exploited the beam diffraction in the negative first order to normalise the VUV laser intensity pulse by pulse and were able to reliably measure absorption signals of $10^{-4}\,5$.

We present here an alternative method to record absorption spectra with high sensitivity that relies on frequency modulation techniques. The VUV radiation is produced by two-photon resonance-enhanced ($\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 \pm \tilde{\nu}_2$) four-wave mixing in Kr using the $^1S_0 \rightarrow 4p^5\,5p[1/2](J = 0)$ resonance at $2\tilde{\nu}_1 = 94\,092.96\,\text{cm}^{-1}$ using the output of two FT-limited pulsed lasers (pulse length $5\,\text{ns}$, obtained by pulse amplification of cw ring laser radiation). The modulation of the VUV laser frequency is achieved by generating side bands on the output of the second laser ($\tilde{\nu}_2$) using an electro optical modulator. These side bands are automatically transferred to the VUV because the four-wave mixing process is linearly dependent on the intensity of the second laser.
Although the torsion and rotation-torsion spectra of several isotopic species of methanol with a symmetrical CH$_3$ or CD$_3$ methyl group was analyzed some time ago, it is recently, and only for the monodeuterated species CH$_2$DOH, that such analyses were extended to the case of an asymmetrical methyl group. In this poster, starting from a far infrared Fourier transform high-resolution spectrum recorded in the 20 to 670 cm$^{-1}$ region and from microwave and terahertz spectra recorded from 75 GHz to 1.5 THz, analyses of the torsion and rotation-torsion spectra of doubly deuterated methanol CD$_2$HOH will be presented. In a first step, the Q branch of torsional subbands were assigned in the far infrared and terahertz spectra with the help of a calculated torsion-rotation spectrum computed with a theoretical approach accounting for the rotation-torsion Coriolis coupling and for the dependence of the generalized inertia tensor on the angle of internal rotation. For many torsional subbands, the rotational structure could be fitted using an effective rotational Hamiltonian expressed as a $J(J+1)$ expansion. In a second step, starting from previously reported microwave data, more than 1000 parallel and perpendicular transitions within the ground torsional state were assigned. The number of torsional subbands assigned in both steps is 74.

In the poster, the torsional parameters retrieved in the analysis of the torsional subband centers will be discussed. The results of the analysis of the rotation and rotation-torsion transitions with the effective rotational Hamiltonian will be presented. The results of the analysis of the same data set with the fitting rotation-torsion Hamiltonian used in the case of the monodeuterated species will also be presented. This last analysis revealed that torsional levels with $K < 3$ are strongly perturbed.

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FULL-DIMENSIONAL QUANTUM DYNAMICS AND SPECTROSCOPY OF AMMONIA ISOTOPOMERS

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Ammonia has been a prototype molecule for spectroscopy and quantum tunneling dynamics for a long time ([1,2] and references cited therein). Recently, accurate full-dimensional potential energy hypersurfaces have become available ([2,3] and references cited therein).

In the present work we have applied and further developed the program GENIUSH ([4] and references therein) for the variational solution of the nuclear Schrödinger equation and the computation and interpretation of vibrational and rotational-vibrational energy levels and wave functions of ammonia isotopomers $^{14}$NH$_3$, $^{14}$NHD$_2$, $^{14}$NH$_2$D, $^{14}$ND$_3$, $^{14}$NHDT, $^{14}$NH$_3$Mu, $^{14}$ND$_3$Mu and $^{14}$NHDMu. The numerical construction of the general and exact kinetic energy operator allows the application of arbitrarily chosen internal coordinates and body-fixed frame embeddings (including the Eckart frame). Our up-to-date version of GENIUSH is able to employ a contracted vibrational basis set containing products of reduced-dimensional vibrational eigenfunctions, which facilitates the computation of highly-excited rovibrational eigenstates. Besides the computation of accurate rotational-vibrational energy levels and wave functions GENIUSH has been extended to include dynamics under coherent infrared multiphoton excitation [5].

References


MOL-D A DATABASE FOR PHOTO-DISSOCIATION CROSS-SECTIONS FOR INDIVIDUAL RO-VIBRATIONAL STATES OF DIATOMIC MOLECULAR IONS

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MOL-D database, developing in Belgrade, is a repository of cross-sections and rate coefficients for specific collisional processes and a web service within the Virtual Atomic and Molecular Data Centre (VAMDC, http://www.vamdc.org) and the Serbian Virtual Observatory (SerVO, http://servo.aob.rs). This database covers photo-dissociation cross-sections for the individual ro-vibrational states of the diatomic molecular ions and rate coefficients for the atom-Rydberg atom chemi-ionization and inverse electron-ion-atom chemi-recombination processes. For the moment it contains data for photodissociation cross-sections of hydrogen $H_2^+$ and helium $He_2^+$ molecular ions and the corresponding average thermal photodissociation cross-sections for the relevant temperature range. Such data are of interest for the use in hydrogen and helium laboratory plasmas research as well as for elaboration of atmosphere models of solar, near solar type stars and helium-rich white dwarf atmospheres.
CHEMI-IONIZATION PROCESSES CAUSED BY THE CREATION OF QUASI-MOLECULAR COMPLEXES IN ATOM - RYDBERG ATOM COLLISIONS

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In this work we will demonstrate that such inelastic processes in atom Rydberg-atom collisions, as chemi-ionization and (n-n') mixing, should be considered together. In this context will be considered the influence of the (n-n') mixing during a symmetric atom Rydberg-atom collisions on the intensity of chemi-ionization process. The considered processes are treated as the result of the almost resonant energy conversion within the electron component of a quasi-molecular complex, created during thermal atom Rydberg-atom collisions. It will be taken into account H(1s) + H*(n) and He(1s²) + He*(n) collisional systems, where the principal quantum number n >> 1, as well as A + A*(n) systems, where A denotes one of the alkali metal atoms. It will be demonstrated that the inclusion of (n-n') mixing in the calculation, influences significantly on the values of chemi-ionization rate coefficients, particularly in the lower part of the block of the Rydberg states. Different possible channels of the (n-n') mixing influence on chemi-ionization rate coefficients will be investigated. The influence of the considered chemi-ionization processes on kinetics within weakly ionized layers of different stellar atmospheres will be demonstrated.
WAVE FUNCTIONS AND LIFETIMES OF OZONE METASTABLE STATES ABOVE THE DISSOCIATION THRESHOLD: IMPACT ON THE DYNAMICS

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The new potential energy surface of ozone recently developed\(^1,2\) is used to determine energies of vibrational bound states and predissociation resonances of O\(_3\). For the vibrational state calculations, the hyperspherical coordinates and the methods of slow-variable discretization with a complex absorbing potential are used\(^3\). Results obtained in this study perfectly agree with previous calculations and reproduce the experimental energies up to the 8000 cm\(^{-1}\) region. Coupling between the three potential wells of the ozone molecule is taken into account, which is important for the correct description of excited vibrational levels and resonances. Symmetric and asymmetric isotopologues can be treated. For symmetric isotopologues, states of all possible irreducible representations have been calculated and widths of the resonances in the region 0-3000 cm\(^{-1}\) above dissociation determined. The widths are mostly between 0.1 cm\(^{-1}\) and 10 cm\(^{-1}\), depending on the nature of the short-range part of the resonance wave functions: Resonances may differ by the degree of vibrational excitation and also by the relative angular momentum of the dissociating O-O\(_2\) system, which can also be viewed as motion between the three potential wells. Wave functions of the predissociation resonances obtained for asymmetric molecules provide information about the exchange reaction \(^1\text{O} + ^3\text{O}^6\text{O} \rightarrow ^1\text{O} + ^3\text{O}^6\text{O}\) or \(^3\text{O} + ^1\text{O}^6\text{O} \rightarrow ^1\text{O} + ^3\text{O}^6\text{O}\). A possible impact on the dynamics will be discussed. This work is supported by the Conseil Régional Champagne-Ardenne (ESRI/Sdel/OD-20130604), National Science Foundation, Grant No PHY-10-68785 and French-Russian LIA SAMIA.

HOT WATER EMISSION SPECTRA: ROTATIONAL ENERGY LEVELS OF THE (000) AND (010) STATES OF HD^{17}O

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In this work we report the current results of our long standing efforts to sample the complete potential energy surface of water isotopologues using the high sensitive HOTGAME (Hot Gas Molecular Emission) spectroscopy experiment in Gießen. We measured the spectra of deuterated and ^{17}O enriched water at a gas temperature of 1950 K in the far-infrared region. For a typical one day measurement the signal to noise ratio of the recorded spectra is better than 3000 at a resolution of 0.005 cm^{-1}. In a wavenumber range of only 200 cm^{-1} we identified 6000 emission lines corresponding to six water isotopologues: H_2^{16}O, H_2^{17}O, H_2^{18}O, HD^{16}O, HD^{17}O, and D_2^{16}O. In this work we present the results regarding transitions involving the HD^{17}O rotational-vibrational energy levels.

For the HD^{17}O isotopologue we assigned 169 emission lines to 189 partly overlapping transitions of pure rotational and the ν_2 − ν_2 rotational bands. A new extended set of 390 rotational energy levels for the (000) and (010) vibration states of HD^{17}O up to J = 17 and K = 13 was obtained by a combination of the new line transitions with those reported in previous studies. We constructed an effective rotational Hamiltonian based on the generation function approach. For this Hamiltonian the deviation between calculated and measured eigenenergies is in the order of 0.001 cm^{-1}. We report a new calculated linelist based on our new energy level list. This linelist supersedes the IUPAC linelist for the HD^{17}O water isotopologue as it is based on a substantially extended set of accurate transition wavenumbers.

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IONIZATION SPECTROSCOPY AND PHOTOPHYSICS OF MOLECULES OF ASTROPHYSICAL AND BIOLOGICAL INTEREST IN THE FAR ULTRAVIOLET: THEORY AND EXPERIMENT

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For many years, our group investigated the vacuum ultraviolet spectroscopy and photophysics of molecules of astrophysical and biological interest. Recently, we have studied acetyl cyanide (CH$_3$C(O)CN)$^1$ and aminoacetonitrile (NH$_2$CN$_2$CN)$^2$ which are key compounds for the prebiotic chemistry occurring in interstellar space. Aminoacetonitrile, for example, is a direct precursor of glycine and has been detected in Sgr B2(N) in 2008. This detection has not been confirmed since, but the compound can be formed by Strecker-type reactions, pathways which constitute a solid scenario for the formation of amino acids in space as has been demonstrated by dedicated space simulation experiments. CH$_3$C(O)CN has not been detected yet in astrophysical objects but its formation needs only bimolecular interaction (for example on grains) of acetaldehyde and HCN, compounds that are highly abundant in interstellar space.

We have also investigated in the past the ionization photophysics of nucleic acid bases and their analogues. This work has been reviewed by us very recently$^3$. This year we have published our work on the photoelectron spec-


troscopy of thymine\textsuperscript{4,5}. The vibrationally resolved spectra of the ion ground and first excited electronic state are analyzed using quantum chemical calculations of the geometry of the involved states. We consider gas phase measurements of biomolecules as particularly necessary since they permit to measure the intrinsic photophysical properties of relevant molecules. Furthermore, comparison to quantum chemical calculations, where in most cases isolated molecules are studied, is straightforward. These studies can be considered as a benchmark for even larger biomolecules.

We present here results obtained with the electron-ion coincidence spectrometer DELICIOUS III available at the DESIRS beamline at Soleil on the above cited molecules. The presentation will insist on the synergy between state-of-the-art measurements and ab-initio quantum chemical calculations that is exemplified in our work.


THE BAND SYSTEM OF ETHANE AROUND 7 MICRON: FREQUENCY ANALYSIS OF THE $\nu_6$ BAND

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High quality line parameters of the band systems of ethane are required for accurate characterization of spectral features observed in the atmospheres of Jovian planets and their satellites. To date, line parameters in the form of line frequencies and absorption cross section for the torsional bands near 35 $\mu$m have been provided.\(^1\), \(^2\) Frequency analysis for $\nu_9$ (820 cm$^{-1}$), $\nu_3$ (990 cm$^{-1}$), $\nu_{12} - \nu_9$ (380 cm$^{-1}$), and $\nu_9 - \nu_4 - \nu_4$ (830 cm$^{-1}$) bands have also been reported.\(^3\) All of these bands occur below 7 $\mu$m region and their frequency analyses have been made within experimental uncertainty. Line parameters and partial assignments have also been provided for the $\nu_6$ and $\nu_8$ bands near 7 $\mu$m \(^4\) as well as the 3.3 $\mu$m region that contains the $\nu_5$ and $\nu_7$ modes.\(^5\) The RMS deviations for the fits in the 7 and 3.3 $\mu$m regions were approximately $5 \times 10^{-3}$ cm$^{-1}$. This is well outside the experimental uncertainty of $<5 \times 10^{-4}$ cm$^{-1}$.

Here, we report an analysis of the $\nu_6$ band near 7.2 $\mu$m (1380 cm$^{-1}$) with frequencies from $\nu_9$, $\nu_3$, $\nu_{12} - \nu_9$, $\nu_9 - \nu_4 - \nu_4$ and the torsional bands. The Hamiltonian model included new couplings between $\nu_6$ and $\nu_9$ (in particular with $\nu_9 + 2\nu_4$ with which it is resonantly coupled) and $\nu_6$ and $\nu_8$ modes. An excellent fit was obtained which will be discussed. We hope to report on a combined frequency analysis of the all of the bands contained in the 7 $\mu$m region and those at longer wavelengths in the near future.

CLASSICAL TRAJECTORY SIMULATION OF LINE MIXING EFFECTS IN ISOTROPIC RAMAN SPECTRA OF PURE NITROGEN: FROM LOW TO HIGH TEMPERATURES

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In the recent paper [1] line mixing effects in dense spectral Q branch of pure N$_2$ isotropic Raman scattering were studied at room temperature using a classical trajectory method. It was the very first study on this subject made using an extended modified version of R.G. Gordon classical theory of impact broadening and shift of rovibrational lines [2]. The whole relaxation matrix was calculated using an exact 3D classical trajectory method for binary collisions of rigid N$_2$ molecules employing the most up-to-date intermolecular potential energy surface [3]. Since the agreement between classical and fully quantum CC/CS relaxation matrices was found excellent, the way is now open to similar studies at low and high temperatures.

In the present work, N$_2$ relaxation matrix is calculated using classical method at several temperatures in the interval between 77 and 2400 K. These data are then applied to calculate the spectra of N$_2$ isotropic Raman Q branch at different pressures from 1 to 10 atm using an efficient algorithm of Gordon and McGinnis [4]. The possible ways of simple approximation of the results obtained are discussed.

REFERENCES
We present the nitrogen dioxide high temperature line list which is allocated on the web site of V.E. Zuev Institute of Atmospheric Optics SB RAS\(^1\). The line list contains the following line parameters: line position, line intensity, energy of lower state and self-broadening coefficient. It is generated using intensity cut off \(10^{-25}\) cm/molecule at 1000 K. This line list covers 466 - 3374 cm\(^{-1}\) spectral range and contains more than one million lines. The line list is based on the global modeling of the line positions and intensities performed within the framework of the method of effective operators\(^2,3\). The parameters of the effective Hamiltonian and effective dipole moment operator have been fitted to the observed values of the line positions and intensities collected from the literature. The used polyad model of effective Hamiltonian takes explicitly into account both the spin-rotation interactions and numerous vibration-rotation resonance interactions arising due to the approximate relations between harmonic frequencies: \(\omega_1 \approx \omega_3 \approx 2\omega_2\). Using this high temperature line list the simulations of low resolution NO\(_2\) spectra have been performed for several spectral regions for two temperatures 296 K and 900 K. The comparison of the spectra at these two temperatures shows the considerable changing of the spectra with the temperature growth.

\(^1\)ftp://ftp.iao.ru/pub/NDDB/
LOW TEMPERATURE BROADENING COEFFICIENTS IN THE $\nu_2$ BAND OF CHLOROMETHANE

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The methyl chloride has, in the later years, taken a special place in atmospheric studies. Following the decrease of CFC-gases production, it became one of the main source of chlorine ions in our atmosphere. As such it plays a major role in the ozone depletion. Its origin is multiple: biomass burnings, tropical forests and human industry. An extensive study of methyl chloride is mandatory to be able to monitor ozone depletion and atmospheric activity.

In this work, we studied the $\text{N}_2$-broadening coefficients in the $Q\text{R}(J,3)$ sub-branch of the $\nu_2$ band of chloromethane. We focused ourselves on low temperatures, from 200 K to room temperature. The spectra were recorded with a high resolution tunable diode laser spectrometer. For each line, at each temperature, we measured the collisional half-width with four different nitrogen pressures, ranging from 12 to 35 mbar.

We retrieved the collisional $\text{N}_2$-broadening coefficients by fitting on the experimental lineshape the Voigt profile and the Rautian and Galatry models, which take into account the Dicke narrowing effect. We then analyzed the temperature and the $J$ dependences of the collisional broadening coefficient. Finally, we compared our results with previous studies.

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MAGNETIC SPIN-TORSION COUPLING IN METHANOL

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The hyperfine structure of non-rigid molecules in which hyperfine coupling arises from equivalent nuclei exchanged by a large amplitude internal rotation is of great interest and leads to unexpected results. In the non-rigid species CD$_3$COH and HCOOCH$_3$, the large amplitude torsional motion of the methyl group leads to hyperfine patterns qualitatively dependent on the A or E nature of the rotation-torsion levels. This stems from the fact that the nuclear spin wavefunction must be such that the total nuclear spin-rotation-torsion wavefunction obeys the Pauli exclusion principle. A quantitative dependence of the hyperfine structure also arises because the hyperfine coupling constants depend on the torsional wavefunction. In methanol, in addition to these effects, the coupling between the large amplitude torsional motion and the hyperfine coupling leads to a less known effect, the so-called magnetic spin-torsion coupling, which was first studied by Heuvel and Dymanus but was not conclusively evidenced at that time. In a recent analysis of the magnetic hyperfine structure of methanol, in which hyperfine patterns recorded for A- and E-type transitions within the ground $v_t = 0$ torsional state were analyzed, a tentative determination of the spin-torsion effects was carried out.

In this poster, based on new spectra recorded using saturated microwave absorption spectroscopy, an analysis of the hyperfine structure of methanol will be undertaken. The magnetic hyperfine coupling Hamiltonian, including spin-rotation, spin-spin, and spin-torsion coupling, to be used for methanol will be presented and the spectroscopic constants involved in these three couplings will be discussed. A line position analysis of the data set considered in the previous analysis and of the new data set will be carried out. The new data set consists of perpendicular rotational transitions within the $v_t = 1$ torsional state; one transition displays a quartet structure, the remaining ones a doublet structure. As the effects of the spin-torsion coupling increase with $v_t$, it is expected that the new data will allow us to carry out a more satisfactory determination of its effects than the previous investigation.


NH$_3$ is commonly used in the analysis of astrophysical environments, and its toxic nature means industrial output must be closely monitored. Both applications require knowledge of high accuracy spectra, for which a vast amount of experimental data is either missing or unassigned. Therefore, accurate theoretical calculations are highly desirable. We report a new ab initio potential energy surface (PES) and dipole moment surface (DMS) to be used in the calculation of rotation-vibration transition frequencies and intensities. Both PES and DMS calculations were performed with the program Molpro using multi reference configuration interaction (MRCI) in the aug-cc-pCVQZ and the aug-cc-pCV5Z basis sets; various choices for the reference space were investigated and relativistic corrections to the energies included. The achieved accuracy of the PES is about 1 cm$^{-1}$ for levels up to 18,000 cm$^{-1}$, which is the most accurate to-date and provides a good starting point for fitting to experimental energy levels. DMS uncertainty is compared to that of BYTe$^2$, and involved comparison of transition intensities with four separate sources of experimental data covering the 900 - 7000 cm$^{-1}$ region. This is particularly important for ammonia in the near infrared. The progress towards generation of a complete linelist on the basic PES and DMS is presented.


Invited Lectures M
Thursday, August 27, 14:00
Chair : B. LAVOREL
ELUCIDATING STRUCTURES OF CARBOHYDRATES BY HIGH RESOLUTION SPECTROSCOPIES (45 min.)

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 Sugars are one of the major building blocks in biology, playing numerous key roles in living organisms. We present several studies on carbohydrates exploiting an experimental strategy which combines microwave, laser spectroscopies in high-resolution, computation and synthesis. Laser spectroscopy offers high sensitivity coupled to mass and conformer selectivity, making it ideal for polysaccharides and glycopeptides studies. On the other hand, microwave spectroscopy coupled with ultrafast laser vaporization provides much higher resolution and direct access to molecular structure of monosaccharides. This combined approach provides not only accurate chemical insight on conformation, structure and molecular properties, but also benchmarking standards guiding the development of theoretical calculations.

In order to illustrate the possibilities of a combined microwave-laser approach we present results on the conformational landscape and structural properties of several monosaccharides,\textsuperscript{1,2} polysaccharides\textsuperscript{3} and glicopeptides including microsolvation and molecular recognition processes.\textsuperscript{4}


ELECTRONIC SPECTRA OF ORGANIC RADICALS AND IONS OF RELEVANCE TO INTERSTELLAR SPACE AND COMBUSTION (45 min.)

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Focus of our research is the measurement of the hitherto unknown electronic spectra of radicals and cations containing mainly carbon atoms, which are of astrophysical and combustion relevance. Initial information on the systems is often obtained by measuring the absorption in 6 K neon matrices using a mass-selected ion beam. In the gas phase the spectra of the neutral radicals are obtained by a resonant two colour photoionisation approach, whereas a radiofrequency trap is used for the cations. The mass-selected ions are restrained there and cooled by collisions with cryogenically cooled helium to 6–20 K prior to the measurement of the electronic transitions. The spectra have been obtained by a one- or two-colour, two-photon excitation-dissociation approach. A method to detect transitions using the difference in the rate of the complex formation with helium in the ground and excited electronic state has been demonstrated. The availability of gas phase spectra allows the in situ monitoring of the transient species in combustion processes and a direct comparison with astronomical observations. Such laboratory measurements at 6 K in the gas phase have led to the first definitive identification of two diffuse interstellar bands to $C_{60}^+$.

Poster Session N
Thursday, August 27, 16:00
WORKING WITH THE HITRAN DATABASE USING HAPI: HITRAN APPLICATION PROGRAMMING INTERFACE

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A HITRAN Application Programing Interface (HAPI [1]) has been developed to allow users on their local machines much more flexibility and power. HAPI is a programming interface for the main data-searching capabilities of the new HITRAN\textsuperscript{online} web service (www.hitran.org). It provides the possibility to query spectroscopic data from the HITRAN [2] database in a flexible manner using either functions or query language. Some of the prominent current features of HAPI are: a) Downloading line-by-line data from HITRAN\textsuperscript{online} b) Filtering and processing the data in SQL-like fashion c) Using conventional Python data structures for representing spectroscopic data d) Possibility to use a large set of third-party Python libraries e) Python implementation of the Hartmann-Tran line profile [3] f) Python implementation of total internal partition sums (TIPS-2011 [4]) for spectra simulations g) High-resolution spectra calculation accounting for pressure, temperature and optical path length h) Providing instrumental functions to simulate experimental spectra i) Possibility to extend the functionality by user’s custom code.

Currently the API is a module written in Python and designed to deal with data in multiple formats such as ASCII, CSV, HDF5 and XSAMS.

This work has been supported by NASA Aura Science Team Grant NNX14-AI55G and NASA Planetary Atmospheres Grant NNX13AI59G.

References
[1] www.hitran.org/hapi
HIGH-RESOLUTION STIMULATED RAMAN SPECTROSCOPY AND ANALYSIS OF $\nu_2$ AND $\nu_3$ BANDS OF of $^{13}$C$_2$H$_4$ USING THE $D_{2h}$ TOP DATA SYSTEM

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High resolution stimulated Raman spectra of $^{13}$C$_2$H$_4$ in the regions of the $\nu_2$ and $\nu_3$ Raman active modes have been recorded at room temperature (296 K) based on the quasi continuous-wave (cw) stimulated Raman spectrometer at Instituto de Estructura de la Materia (CSIC) in Madrid. A tensorial formalism adapted to $X_2Y_4$ planar asymmetric tops with $D_{2h}$ symmetry has been developed in Dijon\(^1\) and a program suite called $D_{2h}$TDS (now part of the XTDS/SPVIEW spectroscopic software\(^2\)) was proposed to calculate their high-resolution spectra\(^3\). The effective Hamiltonian operator, involving a polyad structure, and transition moment (dipole moment and polarizability) operators can be systematically expanded to carry out global analyses of many rovibrational bands. A total of 172 and 65 lines corresponding to $\nu_2$ and $\nu_3$ Raman active modes have been assigned and fitted in frequency with a global root mean square deviation of $2.0 \times 10^{-4}$ cm$^{-1}$ and $2.3 \times 10^{-4}$ cm$^{-1}$, respectively. The figure below shows the stimulated Raman spectrum of the $\nu_2$ band of $^{13}$C$_2$H$_4$, compared to the simulation at 296 K.

MEASUREMENTS AND THEORETICAL MODELLING OF COLLISIONAL LINE-SHAPE PARAMETERS FOR THE $\nu_1 + \nu_3$ BAND OF ACETYLENE PERTURBED BY CARBON DIOXIDE

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The line parameters for the C$_2$H$_2$-CO$_2$ system are needed for studies of planetary atmospheres with acetylene traces and a high content of carbon dioxide. Their temperature dependences are also of crucial impact for radiative transfer modelling.

Using a 3-channel tunable diode laser spectrometer, we recorded C$_2$H$_2$-CO$_2$ spectra in the $\nu_1 + \nu_3$ band region at temperatures in the range 213-333K in order to get the reference-temperature values and the temperature-dependence coefficients. CO$_2$-broadened C$_2$H$_2$ line widths and CO$_2$-induced C$_2$H$_2$ line shifts were deduced with several line-profile models: the traditional Voigt profile as well as the more advanced Speed-Dependent Rautian profile (accounting for hard velocity-changing collisions and speed-dependence of relaxation rates) and correlated Speed-Dependent Rautian profile (assuming the full correlation of both effects). For the room-temperature spectra the line-mixing effects were investigated too.

The CO$_2$-broadened line widths were also estimated theoretically by a semi-empirical (SE) method [1] based on a simplified re-writing of semi-classical expressions under the straight-line trajectory approximation, leading to analytical expressions for the efficiency functions and empirical parameters accounting for the trajectory curvature, corrections to the scattering matrix and vibrational dependence. These SE parameters were first fitted on some measured Voigt-profile line widths and used further to compute the broadening coefficients of all other lines. Moreover, calculations performed at various temperatures with the once fitted SE-parameters enabled deducing of temperature-dependence exponents. Both calculated reference-temperature line-widths and their temperature-dependence exponents were found to be in a very good agreement with our own measurements and other data available in the literature.
HIGH RESOLUTION ANALYSIS OF THE ETHYLENE–$^{13}$C SPECTRUM IN THE REGION 600-1700 CM$^{-1}$

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We report the results of highly accurate ro-vibrational analysis of the $\nu_2$, $\nu_3$, $\nu_4$, $\nu_7$, $\nu_8$, $\nu_{10}$, and $\nu_{12}$ bands of the ethylene–$^{13}$C ($^{12}$C$^{13}$CH$_4$) in the region 600–1700 cm$^{-1}$. The $^{12}$C$^{13}$CH$_4$ is an asymmetric top molecule with the symmetry isomorphic to the $C_{2v}$ point symmetry group.

In the present study the infrared spectra of $^{12}$C$^{13}$CH$_4$ were recorded using a Bruker IFS 125 HR Fourier transform spectrometer with a resolution of 0.0063 cm$^{-1}$ at Nanyang Technological University, Singapore. More than 10 000 transitions with maximum values of quantum numbers $J_{\text{max}} = 22, 15, 36, 47, 30, 47$ and $K_a^{\text{max}} = 8, 5, 22, 10, 15$ were assigned to the $\nu_2$, $\nu_3$, $\nu_4$, $\nu_7$, $\nu_8$, $\nu_{10}$, and $\nu_{12}$ bands, respectively. Two weak bends, $\nu_2$ and $\nu_3$, were recorded and analyzed for the first time.

Known in the literature rotational and centrifugal distortion parameters of the ground vibrational state were improved on the basis of assigned transitions. The set of parameters obtained from the fit reproduces the initial infrared data within accuracies close to experimental uncertainties.
HIGH RESOLUTION ANALYSIS OF THE C$_2$H$_2$D$_2$-TRANS MOLECULE IN THE REGION OF 1400-2000 CM$^{-1}$

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The C$_2$H$_2$D$_2$-trans isotopologue is a nearly prolate asymmetric top molecule and belongs to the C$_{2h}$ point symmetry group. Twelve vibrational modes exist and their vibrational states can be divided in four different symmetries, $A_g$, $A_u$, $B_g$, and $B_u$. Only vibrational states of $A_u$ and $B_u$ symmetry are allowed in absorption for transitions from the ground vibrational state.

We present an analysis of a set of weak combination bands below 2000 cm$^{-1}$ ($v_8 + v_{10}$ ($A_u$), $v_6 + v_{10}$ ($B_u$), $v_6 + v_7$ ($A_u$), $v_3 + v_{10}$ ($B_u$), $v_4 + v_6$ ($A_u$)) taking into account strong Coriolis and Fermi resonance interactions. The experimental spectrum of C$_2$H$_2$D$_2$-trans in the 1400-2000 cm$^{-1}$ region was recorded with the Fourier-transform spectrometer IFS-120 HR at Technische Universität Braunschweig at room temperature with a pressure of 0.62 mbar, an absorption path length of 16 m and an optical resolution of 0.0025 cm$^{-1}$.

Such an analysis of the five weak bands was made for the first time. A set of obtained parameters reproduces the initial experimental energy levels with an accuracy close to experimental uncertainties.
FOUR YEARS OF THE EXOMOL PROJECT: MOLECULAR LINE LISTS FOR EXOPLANET AND OTHER HOT ATMOSPHERES


Fundamental molecular data play a key role for spectral characterization of hot astrophysical objects cool enough to form molecules in their atmospheres as well as in a broad range terrestrial applications. However laboratory data for key species is absent, inaccurate or incomplete. The ExoMol project aims to provide comprehensive line lists for all molecules likely to be observable in exoplanet atmospheres in the foreseeable future.\(^1\) This is a huge undertaking which will mean computing in excess of a hundred billion spectral lines and dealing with a large variety of molecular species.\(^2\) Line lists currently available from ExoMol (www.exomol.com): NH\(_3\), CaH, MgH, BeH, SiO, HCN/HNC, KCl, NaCl, CH\(_4\), AlO, H\(_2\)CO, ScH, PH\(_3\), PN, HNO\(_3\) and CS.\(^3\) Line lists currently under construction include those for SO\(_2\), SO\(_3\), AlH, C\(_2\), C\(_3\), C\(_2\)H\(_2\), SH, SiH, CaO, CrH, TiH, VO, CH\(_3\)Cl, H\(_2\)S and C\(_2\)H\(_4\). We will present examples of molecular spectra computed using the ExoMol line lists.

This work is part of the ExoMol project supported by the ERC under Advanced Investigator Project 267219.

\(3\) S.N. Yurchenko, R.J. Barber, J. Tennyson, \textit{MNRAS}, \textbf{413}, 1828 (2011) DOI
\(12\) C. Sousa-Silva et al, \textit{MNRAS}, \textbf{446}, 2337 (2014) DOI
THE NUCLEAR SPIN CONVERSION RATE OF CH\textsubscript{4} IN A Kr MATRIX MEASURED BY FTIR SPECTROSCOPY

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A CH\textsubscript{4} molecule has four protons, so that the total nuclear spin \(I\) is 0, 1, or 2. According to the Pauli exclusion principle, the rotational state of \(J=0\) combines with the nuclear spin states of \(I=2\), \(J=1\) with \(I=1\), and \(J=2\) with \(I=0\) or \(I=1\). Considering these specific combinations, some authors have studied nuclear spin conversion of CH\textsubscript{4} trapped in various rare gas matrices by infrared spectroscopy.\textsuperscript{1,2} In this study, we investigated temperature dependence of the conversion rate of CH\textsubscript{4} trapped in a Kr matrix to clarify the conversion mechanism.

A vacuum chamber equipped with a cryostat was evacuated to \(1.0 \times 10^{-8}\) Pa. We used a Cu substrate coated with a vacuum-evaporated gold film. CH\textsubscript{4} and Kr gases were blended in a gas handling line, and then sprayed thorough a variable leak valve to the substrate cooled by liquid He. After condensation, samples were annealed at about 40 K, and were then rapidly cooled down. Infrared light was detected with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. Infrared absorption spectra were measured at resolutions of 0.5 and 1.0 cm\textsuperscript{-1} in the reflection configuration with the incident angle of 80\textdegree.

Infrared absorption spectra of CH\textsubscript{4} trapped in a Kr matrix indicated rotational splitting of the \(\nu_4\) absorption band after annealing. With increasing time, the intensity of the R(0) branch increased, whereas the intensities of the P(1), Q(1), and R(1) branches decreased. This rotational relaxation from \(J=1\) to \(J=0\) means nuclear spin conversion from \(I=1\) to \(I=2\). From the analysis of the time evolution of vibrational-rotational spectra, the conversion rates were determined at several temperatures. For instance, the rate at 7.6 K was estimated at \(6 \pm 1\) h\textsuperscript{-1}. We will also compare the rate in a Kr matrix with that in a Xe matrix. Based on the obtained temperature- and matrix-dependence of the conversion rate, we will discuss the mechanism of the nuclear spin conversion of CH\textsubscript{4} in rare gas solids.

FTIR SPECTROSCOPY OF D$_2$O CLUSTERS ISOLATED IN SOLID RARE GAS MATRICES

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The stable structures of water clusters have been investigated for several decades. The spectroscopic investigations of D$_2$O clusters have been performed in gaseous phase and in various matrices: Ne, Ar, Kr, and para-H$_2$. It is difficult to correctly assign infrared absorption peaks to a variety of OD stretch modes in the clusters of various sizes, based only on comparisons of their frequencies with the calculated ones. In the present study, we measured infrared spectra of D$_2$O clusters in argon matrices, and made reliable assignments taking into account D$_2$O-concentration dependence of the spectrum. Moreover, we investigated temperature- and matrix-dependence of the spectrum in order to reveal the size-growth processes of water clusters and effects of rare gas matrix species on the vibrations of the clusters, respectively.

The experimental apparatus consists of an ultrahigh vacuum (UHV) chamber with a liquid helium cryostat, a Fourier transform infrared (FTIR) spectrometer, and a compartment of an external HgCdTe detector. The base pressure of the UHV chamber was $1 \times 10^{-8}$ Pa. The substrate was a gold film vacuum-evaporated on an oxygen-free copper. The temperature of the substrate was 7.5 K. The gas mixture of D$_2$O and rare gas was prepared in a gas handling system, and was effused from a small orifice directed to the substrate. FTIR measurements were carried out at a spectral resolution of 2 cm$^{-1}$ in reflection configuration. The incident angle of p-polarized infrared light was 80$^\circ$.

Infrared spectra of D$_2$O in argon matrices at 7.5 K showed absorption peaks at 2658 cm$^{-1}$ ($\alpha$), 2653 cm$^{-1}$ ($\beta$), 2635 cm$^{-1}$ ($\gamma$), and 2614 cm$^{-1}$ ($\delta$). The $\alpha$ peak is assigned to the symmetric stretch ($\nu_1$) of the non-rotating monomer, and $\delta$ to the bonded OD stretch in the dimer. Ceponkus et al. assigned $\beta$ to $\nu_1$ of deuton-acceptor D$_2$O in the dimer, but $\beta$ appeared also in the spectrum at a low concentration of D$_2$O (Ar/D$_2$O=100), where the dimer peak $\delta$ was not observed. Therefore, we attributed the $\gamma$ peak, which arised together with

δ, to ν₁ of deuton-acceptor D₂O in the dimer instead. On the other hand, the β peak close to α was assigned to ν₁ of the rotating monomer. Thus, we made assignments of the infrared absorption peaks, considering the concentration-dependence of the spectrum. In the presentation, we will discuss the cluster growth processes and configurations of surrounding rare gas species, based on the measurements of temperature- and matrix-dependence of the spectrum, respectively.
DETERMINATION OF EXCITED STATE DIPOLE MOMENTS VIA ELECTRONIC STARK SPECTROSCOPY: 5-METHOXYINDOLE

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The dipole moments of electronically excited states may differ considerably from those of the ground state, as a consequence of the altered electron distribution upon excitation. This change of the dipole moment upon electronic excitation has a large influence on solvation dynamics, which is largely governed by the interactions of solute and solvent dipole moments.

The excited state dipole moment of the lowest electronically excited singlet state of 5-methoxyindole has been determined by means of optical Stark spectroscopy in a molecular beam. The resulting spectra at different field strengths and with different optical selection rules are fit using an automated evolutionary algorithm approach. We find a slight reduction of the absolute dipole moment from 1.58(5) D to 1.21(5). At the same time, the direction of the dipole moment orientation rotates by 60° showing the importance of the determination of the dipole moment components, along with the absolute values.

For the electronic ground state, the dipole moment vector of anti-5MOI can be constructed from a vector addition of the methoxy group and the indole dipole moment vectors with good accuracy, showing the influence of induction to be small. This procedure completely fails for the lowest excited singlet state. Electronic excitation leads to a shift of electron density in the chromophore, which is partially accompanied by an electron density shift from or to the chromophore. Depending on the acceptor or donor properties of the substituents and even more on the electronic nature (mesomeric or inductive substituents) the concept of vector addition of bond or group dipole moments complete fails for excited states.

In many molecules it is possible to determine the direction of the transition dipole moment from the frontier orbitals. However, when strong σ effects govern the electron density distribution after excitation, great care has to be exercised, not to overstress the fundamental rules, which are based on electron density effects in the π-space in case of the frontier orbitals.

The charge migration upon electronic excitation shows a net charge flow from the pyrole to the benzene ring as in comparable 5-substituted indoles. While for the methoxy π electrons the electron density decreases (it is shifted into the
chromophore), the $\sigma$ density at the methoxy O atom increases upon electronic excitation. There is an opposite charge flow observed for the $\sigma$ electrons compared to the $\pi$ electrons also for the carbon and nitrogen atoms in the indole chromophore.
AN EFFICIENT ALGORITHM FOR A HIGH-PRECISION H₂ ENERGY CALCULATION WITH AN EXPONENTIALLY CORELATED BASIS

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In order to obtain highly accurate nonrelativistic energies and quantum electrodynamics corrections in molecular systems, a well-optimized basis set is needed. Especially if the QED corrections of $m \alpha^6$ order are to be calculated. The usual approach, using correlated Gaussian basis (ECG), provides relatively simple algorithms. However, the Gaussian functions do not satisfy Kato’s cusp condition. This can lead to unsatisfactory convergence at this level of precision and even to wrong results, as in case of a $\delta'$ operator. Therefore, exponentially correlated exponential functions are to be considered:

$$\psi = e^{-tr_{12} - u(r_{1A} + r_{1B}) - u(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B})},$$

where $r_{ij}$ denotes distance between $i$ and $j$, subscripts 1 and 2 denote electrons, $A$ and $B$ - nuclei. These functions involve all possible correlation terms and do not possess the disadvantages of Gaussians. The main problem of such basis are two-centre integrals which are difficult to solve. An efficient algorithm, based on a Taylor expansion\(^1\) is presented. The integrals are expanded in an absolutely convergent series in an internuclear distance $r$. The series converges as $\frac{1}{r^8}$, allowing all the integrals to be computed for any value of $r$. Recurrence relations between the series coefficients are shown. As the recursions are unstable for certain range of the $t$ parameter (Eq. 1), a way to overcome this issue is also presented, together with the results of an exemplary H₂ Born - Oppenheimer ground state calculation.

GROWTH PROCESSES OF D$_2$O CLUSTERS IN A CH$_4$ MATRIX OBSERVED BY FTIR SPECTROSCOPY

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The experimental and theoretical efforts have revealed stable structures and rovibrational properties of water clusters with various sizes.$^{1,2}$ On the other hands, the growth processes of water clusters have not been investigated in detail. In the previous study, we found (D$_2$O)$_n$ clusters with $n$=2-4 in a CH$_4$ matrix.$^3$ We are investigating the growth of the clusters in solid CH$_4$ induced by annealing. In contrast to rare gases and homonuclear diatomic molecules as hosts, a CH$_4$ molecule has an advantage of having infrared-active vibrational modes ($\nu_3$ and $\nu_4$). Measuring infrared absorption of CH$_4$ in addition to that of (D$_2$O)$_n$, we probe the geometrical structure of the host, and reveal how the host affects the structures and vibrational properties of the clusters.

An ultrahigh vacuum (UHV) chamber equipped with a liquid helium cryostat was degassed at 373 K for 24 hours, and the base pressure of $1\times10^{-8}$ Pa was obtained after the baking process. A gold-coated oxygen-free copper substrate was attached to the cryostat and was cooled to 7.5 K. The gas mixtures of D$_2$O and CH$_4$ prepared in a gas handling system were introduced into the UHV chamber through a variable leak valve, and were condensed on the substrate. Infrared spectra were measured at a resolution of 2 cm$^{-1}$ with a FTIR spectrometer and a HgCdTe detector. The reflection geometry was used, and the incident angle of infrared light was 80°.

Before annealing, the bonded-OD absorption feature of the D$_2$O dimer appeared around 2595 cm$^{-1}$ as a shoulder of the $2\nu_4$ peak of amorphous CH$_4$. We also observed the strong and broad $\nu_3$ peak of amorphous CH$_4$ at 3013 cm$^{-1}$. After annealing at 20 K for 6 min, three new absorption peaks were found in the bonded-OD vibration region; the two peaks at 2585 cm$^{-1}$ and 2562 cm$^{-1}$ are due to the trimer, while the other at 2477 cm$^{-1}$ is due to the tetramer, as reported in our previous study.$^3$ We observed the splitting of the $\nu_3$ peak of CH$_4$ at the same time. This means the formation of phase II crystalline CH$_4$, where two kinds of CH$_4$ molecules exist; the librating molecules and nearly-free rotating ones.$^4$ An absorption peak at 3011 cm$^{-1}$ is due to the former, while peaks at 3021 cm$^{-1}$ and 3026 cm$^{-1}$ are due to the latter.

$^3$N. Ehara et al., VASSCAA-7, Hsinchu, Taiwan (2014).
We will discuss dependence of the cluster-size-distribution of D₂O clusters on the annealing duration and temperature, and the relation between vibrational frequencies of the clusters and the structure of the CH₄ matrix.
NEW ACCURATE WAVENUMBERS OF H$^{35}\text{Cl}^+$ AND H$^{37}\text{Cl}^+$ ROVIBRATIONAL TRANSITIONS IN THE $v = 1 \leftarrow 0$ BAND OF THE $^2\Pi$ STATE

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HCl$^+$ is a key intermediate in the interstellar chemistry of chlorine. It has been recently identified in space from Herschel spectra$^1$ and it has also been detected in the laboratory through its optical emission$^2$, infrared$^3$ and mm-wave spectra$^4$. Now that Herschel is decommissioned, further astrophysical studies on this radical ion will likely rely on ground-based observations in the mid-infrared. We have used a difference frequency laser spectrometer coupled to a hollow cathode discharge to measure the absorption spectrum of H$^{35}\text{Cl}^+$ and H$^{37}\text{Cl}^+$ in the $v = 1 \leftarrow 0$ band of the $^2\Pi$ state with Doppler limited resolution. The accuracy of the individual measurements ($\sim$10 MHz (3σ)) relies on a solid state wavemeter referenced to an iodine-stabilized Ar$^+$ laser. The new data are being fit using the CALPGM software from JPL, and the current status will be presented.

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$^2$W. D. Sheasley and C. W. Mathews, J. Mol. Spectrosc. 47, 420 (1973)
HIGH PRESSURE CAVITY RING DOWN SPECTROSCOPY: APPLICATION TO THE ABSORPTION CONTINUUM OF CO2 NEAR 1.7 MICRONS

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A Cavity Ring Down Spectrometer has been developed for high sensitivity absorption spectroscopy at pressure up to 10 bars in the near infrared. In order to strictly avoid perturbations of the optical alignment by pressure forces, the pre-aligned CRDS cavity is inserted inside the high pressure cell. We present here the first application of this newly developed CW-CRDS spectrometer to the study of the room temperature spectrum of CO2 at high pressure. The spectra were recorded between 5850 and 5950 cm⁻¹ for a series of pressure values up to 6400 Torr. The studied spectral interval corresponds to the high energy range of the 1.75 µm transparency window of CO2 of particular interest for Venus. The stability of the spectra baseline was checked by injecting Ar and N2 up to 10 atm. The CO2 absorption coefficient at a given pressure value was obtained as the increase of CRDS loss rate from its value at zero pressure. The CO2 absorption spectrum includes the contribution of the self broadened local rovibrational lines and of a broad and weak continuum. The CO2 continuum was obtained after subtraction of the local lines obtained from a simulation based on the CO2 HITRAN line list and a (truncated) Voigt profile. The pressure dependence of the absorption continuum was checked to be quadratic with an average cross section value on the order of 8 × 10⁻⁹ cm⁻¹ atm⁻² in the studied spectral interval. The derived continuum shows an unexpected spectral feature located in the region of a band ¹⁶O¹²C¹⁸O (present in natural abundance) which dominates the spectrum in the region. This spectral feature, due to collisional interferences between local lines was quantitatively accounted for using a theoretical approach based on the impact and Energy Corrected Sudden (ECS) approximations.
THE WATER DIMER INVESTIGATED IN THE 2OH OVERTONE RANGE USING CAVITY-RING DOWN SPECTROSCOPY

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We have recorded water dimer absorption around 7250 cm\(^{-1}\) using cw-cavity ring-down spectroscopy in both Bruxelles (ULB) and Rennes (IPR). Data are characterized by significantly higher instrumental resolution, about 1MHz as compared to 0.2 cm\(^{-1}\) in the previous gas phase literature\(^1\), as demonstrated in preliminary reports from ULB\(^2\). Slightly different set-ups\(^2,3\) were used and slightly different, partly overlapping energy ranges were scanned at IPR and ULB. Previously reported and assigned\(^1,4,5\) and also new absorption features were observed. Assignments will be discussed and extended, on the basis of partial rotational analyses whenever possible.

**FT EMISSION SPECTRA OF THE DEUTERATED AND $^{17}$O ENRICHED WATER BETWEEN 320 AND 530 CM$^{-1}$**

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One of the most amazing current developments in astrophysics are the spectroscopic studies of hot astronomical objects based on their molecular spectra. To support the chemical analytics of hot water we recorded the laboratory emission spectra of all water isotopologues covering the complete infrared region. In this work we report the analysis of the spectra recorded in the far-infrared region for the deuterated and $^{17}$O enriched water sample at a gas temperature of 1950 K. For a typical one day measurement the signal to noise ratio of the recorded spectra is better than 3000 at a resolution of 0.005 cm$^{-1}$. In a wavenumber range of only 200 cm$^{-1}$ we identified 6000 emission lines of six water isotopologues: H$_2^{16}$O, H$_2^{17}$O, H$_2^{18}$O, HD$^{16}$O, HD$^{17}$O, and D$_2^{16}$O. The results regarding transitions involving the HD$^{17}$O rotational-vibrational energy levels have been published recently.

In this work we present the results for the HD$^{16}$O species based on 1000 newly observed transitions. We extended substantially the results of the single study reported so far for HD$^{16}$O in the 380 – 530 cm$^{-1}$ region. The use of highly accurate variational calculations and previously known experimental energy levels accumulated in the IUPAC TG databases (see references quoted therein) simplified considerably the assignment of these very dense spectra.

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We will present the results regarding the assignment of the emission lines and will discuss the procedures used to calculate the energy levels.
The [H,C,N] molecular system is an important prototypical double well system of molecular physics. The bending states at the H-CN respective CN-H sides of the isomerization barrier merge into the internal rotation states of the hydrogen atom around the CN core as the excitation is increased above the isomerization barrier. In this work we study the connection between the internal dynamics above and below the isomerization barrier. Our eigenstate data set is a spectroscopically assigned eigenenergy spectrum extended for this study up to 23000 cm$^{-1}$ above the HCN minimum. As the vibrational excitation energy approaches the isomerization barrier, the spacing of the vibrational energies shows a vibrational angular momentum dependent Dixon-dip-like trend$^1$, which correlates with the semiclassical pattern of the level spacings$^2$. Based on the level spacings we can determine the dynamical proximity of an eigenstate to the effective dynamical isomerization barrier$^3$. The barrier proximal “saddle point states” are found to be highly localized$^4$ in the bending coordinate at the saddle point as expected from a semiclassical point of view. The localization takes place not only for pure bending states but also at all higher energies, exactly when the eigenenergies match the effective barrier height. The assignments of the levels above the barrier of isomerization connected


$^4$G. Ch. Mellau et all. in prep. (2015) →
to the localized states allows us to obtain the dynamical description of the internal rotation states.
ELECTRONIC STATES OF Rb₂. AB INITIO PREDICTIONS, AND OBSERVATION OF THE 5¹Σ⁺ₜ AND 5¹Πₜ STATES BY POLARIZATION LABELLING SPECTROSCOPY

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Two-colour polarization labelling experiments performed in Warsaw have explored the excitation spectrum of the rubidium dimer in the region 25500 - 27000 cm⁻¹, probing two mutually interacting states, identified from ab initio calculations as the 5¹Σ⁺ₜ and 5¹Πₜ states. Their atomic dissociation products are Rb(5s) + Rb(5d). Treating the rather irregular progressions observed in the excitation spectra as transitions to single states with (numerous) local perturbations, we propose spectroscopic parameters and potential energy curves to describe the investigated levels. Observations cover more than 20 vibrational levels in the inner minima of both the 5¹Πₜ and 5¹Σ⁺ₜ states. Analysis was guided by ab initio calculations¹ performed to describe the 1,3Λ₉,ₜ electronic states of Rb₂ up to the Rb(5s) + Rb(5f) atomic asymptote.

¹The ab initio work was performed with the high performance computational resources of the FLMSN, “Fédération Lyonnaise de Modélisation et Sciences Numériques”, partner of EQUIPEX EQUIP@MESO. We also wish to acknowledge financial support for this collaboration from the PAN-CNRS exchange programme.
DUAL-LASER ABSORPTION SPECTROSCOPY OF C$_2$H$_2$ AT 1.4 $\mu$m

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Non-methane hydrocarbons into the urban atmosphere play an important role in the atmospheric chemistry of OH radicals, ozone and other oxidants. Because of their significant influence on the Earth’s climate, vertical profiles of these trace gases is particularly relevant. Among them, acetylene is the one that is used as reliable tracer for anthropogenic emissions, since it is almost solely derived from combustion. Acetylene is also an important trace constituent of the atmosphere of other planets, like Titan and Saturn. Furthermore, it has attracted the interest of the International Community for Weights and Measures because of its relatively strong absorption features in the International Telecommunication Union’s C band (1530-1560 nm). In fact, a large variety of C$_2$H$_2$ lines can act as reference transitions for the important field of optical telecommunications.

In this work, we report on our determinations of spectroscopic parameters (line intensity factors, self-broadening and self-shifting coefficients) of C$_2$H$_2$ at 1.4 $\mu$m. To this goal, a dual-laser approach was applied, based upon the technique of optical phase-locking, which allowed us to produce an absolute frequency scale underneath the absorption spectra. A pair of extended-cavity diode lasers were used. One of them, the probe laser, is forced to maintain a precise frequency-offset from a reference laser. The optical phase-locking loop reduces the width of the beat-note between probe and reference lasers down to the Hz level, thus demonstrating the narrowing of the probe laser at the level determined by the spectral purity of the reference laser. This latter is an optical frequency standard based on noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICEOHMS) at 1.4 $\mu$m. Laser-gas interaction takes place inside an isothermal multiple-reflection cell, that is stabilized at the temperature of the triple point of water. The unprecedented fidelity in the observation of the shape associated to a given C$_2$H$_2$ vibration-rotation transition allowed us to reach an unprecedented level of accuracy in the measurement of the spectroscopic parameters.
Climate change is one of the greatest challenges presently facing mankind, and methane is one of the most powerful anthropogenic greenhouse gases. In this context, a satellite dedicated to the measurements of atmospheric methane is under joint development by the French and German space research centers (CNES and DLR). The so-called MERLIN mission (Methane Remote Sensing Lidar Mission, 2019) aims at providing global information on atmospheric methane concentration (methane column density) with a relative uncertainty less than 1% and with a spatial resolution of 50 km along the measurement track under cloudy and variable-solar illumination conditions. Such spectroscopic monitoring of gases in the atmosphere of the Earth, requires a precise description of absorption lines shapes that goes beyond the usual Voigt profile (VP). In the case of methane, the differences between the measured profiles and those given by the VP can be very important, making the VP completely incompatible with the reliable detection of sources and sinks from space. These differences are due to various collisional effects between molecules that are neglected by the VP: collisional interference between the lines (line-mixing), collision-induced velocity changes (Dicke narrowing effect) and speed dependence of the collisional broadening and shifting. In this work, we present the first results on the modeling of methane lines broadened by air in the 1.64 µm region and the associated spectroscopic parameters, taking into account all of these collisional effects. These results were obtained by simultaneously fitting the model parameters to high sensitivity and high-resolution cavity ring-down spectroscopy (CRDS) spectra recorded at the NIST and tunable diode laser spectra recorded at the GSMA (Reims), over a wide pressure range (5 to 100 kPa). These spectroscopic data and the associated model to calculate the spectrum absorption coefficient will be then used to analyze...

ground-based atmospheric spectra at the TCCON facility in Park Falls, Wisconsin.
THE PREDICTED SPECTRUM OF THE SbH$_2$ MOLECULE IN ITS LOWEST TWO RENNER-DEGENERATE ELECTRONIC STATES $\tilde{X}$ $^2$B$_1$ AND $\tilde{A}$ $^2$A$_1$

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We continue previous work on the NH$_2$\textsuperscript{1} and PH$_3$\textsuperscript{2} radicals by predicting theoretically the rovibronic absorption spectrum associated with the $\tilde{X}$ $^2$B$_1$ and $\tilde{A}$ $^2$A$_1$ electronic states of the SbH$_2$ molecule. The potential energy and dipole moment surfaces of $\tilde{X}$ $^2$B$_1$ and $\tilde{A}$ $^2$A$_1$ SbH$_2$ have been calculated by the FV-CAS-MRSDCI \textit{ab initio} method. At linear geometries, the two electronic states correlate with a $^2\Pi$ state, and so they are Renner-degenerate. We find evidence of an avoided crossing at bent geometries of the $\tilde{A}$-state potential energy function (PEF) with the PEF of a higher-lying $^2$B$_2$ state. This avoided crossing is analogous to that found for AsH$_2$ by Alekseyev, Buenker, and Liebermann.\textsuperscript{3} We empirically adjust the $\tilde{A}$-state PEF to obtain an approximate diabatic PEF and, using the parameters of the actual $\tilde{X}$-state PEF together with those of the approximate diabatic $\tilde{A}$-state PEF as input, we employ the RENNER program\textsuperscript{4,5} to simulate the rovibronic absorption spectrum. Further details will be given at the conference together with results of the calculations.

MICROWAVE SPECTROSCOPY OF CAMPHENE

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The emission of volatile organic compounds, VOC, from plants have strong relevance for plant physiology, plant ecology and atmospheric chemistry\textsuperscript{1}. Camphene (C\textsubscript{10}H\textsubscript{16}) is one of several monoterpenes which are emitted in the atmosphere by biogenic sources\textsuperscript{2 3}.

The pure rotational spectra of camphene was investigated for the first time using the Microwave Fourier Transform (SIMO) spectrometer of Lille in the 2-20 GHz range. For this bicyclic molecule only one conformer can be observed, and rotational transitions were observed up to J, K\textsubscript{a} = 6, 5. These transitions (N=83) were fit to a Watson A-reduction Hamiltonian with Pickett’s SPFIT program to obtain an rms value better than 2 kHz using a-, b- and c-type transitions. In addition we have recorded in natural abundance the spectra of all ten $^{13}$C isotopomers of camphene. A hyperfine structure was observed. It was associated with the spin-spin interaction of the hydrogen nuclei of the four CH\textsubscript{2} groups of the molecule and modeled to reproduce the observed splittings. All the experimental results were supported by several quantum calculations performed at different levels of theory DFT (B3LYP/6-311++G(2df,p)) and ab initio (MP2/6-311++G(d,p)) using the Gaussian 09 software package and the PhLAM High-Performance computing Linux cluster.

The CaPPA project (Chemical and Physical Properties of the Atmosphere) is funded by the French National Research Agency (ANR) through the PIA (Programme d’Investissement d’Avenir) under contract ANR-10-LABX-005.

SENSITIVITY OF ISOTOPIC LIH ROTATION AND ROTATION-VIBRATION TRANSITIONS TO A VARIATION OF PROTON-TO-ELECTRON MASS RATIO CONSTANT

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Rotation and rotation-vibration transitions of closed shell diatomic molecules are convenient probes to observe a possible variation of the proton-to-electron mass ratio constant $\mu = m_p/m_e$ at cosmological timescales that is predicted by the modern physics $^1$. A strategy was to compare frequencies of molecular lines recorded in laboratory and corresponding lines detected in astrophysical objects at high redshift. A fractional variation of $\mu$ leads to a fractional variation of a molecular frequency $\delta f/f = K_{\mu} \delta \mu/\mu$ determined by the sensitivity coefficient $K_{\mu}$. LiH rotational transition $J = 0 \rightarrow 1$ in the vibrational level $v = 0$ has been detected in the microwave spectra of B0218+357 quasar at $z = 0.68$ $^2$. LiH rotation-vibration transitions have been searched in its forming regions at high redshift $z \approx 200$ $^3$.

Calculations of the sensitivity coefficients for rotation and rotation-vibration transitions of isotopic LiH are presented using the Dunham expansion of energy levels using a set of parameters with Born-Oppenheimer corrections $^4$ for transitions up to $J = 30$ and $v = 3$. Near-resonant transitions arising from the cancellation of rotational intervals with frequency shifts associated to the isotope effect, the anharmonicity or the rotation-vibration interaction display a frequency splitting with an enhanced sensitivity coefficient comparing to that of a transition. Comparison of frequency splittings defined between rotational transitions of isotopic CO and LiH $J = 0 \rightarrow 1$ transition with ammonia inversion transitions detected in B0218+357 allowed to put constraints on the variation of $\mu$.

A NEW TREATMENT OF THE $\nu_4$ AND $2\nu_4$ ROVIBRATIONAL BANDS OF PF$_3$ AROUND 347 cm$^{-1}$ AND 693 cm$^{-1}$

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The high-resolution FTIR spectra of phosphorus trifluoride PF$_3$ have been reinvestigated in the vibrational excited states $\nu_4 = 1$ near 347 cm$^{-1}$ [1] and $2\nu_4 = 1$ near 693 cm$^{-1}$ [2]. Thanks to recent pure rotational measurements, 595 new infrared transitions of the $\nu_4$ band have been assigned extending the rotational quantum-number values to $J_{\text{max}} = 67$ and $K_{\text{max}} = 66$. A merge of the IR transitions and the MW-MM-RF data within the $\nu_4 = 1$ excited level yielded an accurate equilibrium rotational ground state [3] $C_e$ value, 0.16088676 (69) cm$^{-1}$ and $B_e$ value, 0.26177751 (7) cm$^{-1}$, which were used to derive, as for NF$_3$ [4], the equilibrium geometry of PF$_3$, $r_e$(P-F) = 1.560986 (43) Å and $\angle_e$(FPF) = 97.566657(64)$^\circ$. All experimental data of $\nu_4$ have been refined applying the D-, Q- and QD-reduction forms of the rovibrational Hamiltonian. The experimental data of $2\nu_4^0$ and $2\nu_4^2$ components of PF$_3$ have been refined using five equivalent D-, Q-, L-, QD- and LD-reduction forms of the effective Hamiltonian. The body of data comprised 1171 IR lines of $2\nu_4^0$ component, 249 energies of the $\nu_4 = 2$ excited level deduced from $2\nu_4^2 - \nu_4^{-1}$ hot band and 5 reported MW data. The unitary equivalence of the relations between the derived parameters of the $\nu_4 = 1$ and $\nu_4 = 2$ excited states was satisfactorily fulfilled.

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Hydronium plays an important role in planetary and interstellar chemistry\(^1\). This molecular ion is found to exist abundantly in both diffuse and dense molecular clouds as well as in comae. Moreover \(\text{H}_3\text{O}^+\) is a good water indicator and can be used to estimate its abundance when the direct detection is unfeasible\(^2\).

In the present work a theoretical study of the ro-vibrational states of the hydronium ion and its isotopologues is carried out. The potential energy surface (PES) and the dipole moment surface (DMS) for the ground electronic states of \(\text{H}_3\text{O}^+\) were calculated \textit{ab initio} at the full-valence multi-reference single and double excitation configuration level of theory including all electrons with aug-cc-pwCV5z and aug-cc-pwCVQz basis sets, relativity corrections and complete basis set extrapolation. PES and DMS were generated on an extended grid of geometries and fitted to symmetrized analytical functions. Then these functions were used to calculate ro-vibrational energy levels, wavefunctions and Einstein coefficients of the systems under consideration employing the TROVE program\(^3\). Finally the cooling rates were estimated and analyzed.

We will present a detailed analysis of the stability of the ro-vibrational states of \(\text{H}_3\text{O}^+\), \(\text{HD}_2\text{O}^+\) and \(\text{D}_3\text{O}^+\) and identify the most long-living states of these ions.

\(^1\)doi:10.1086/317137, M.J. Jensen, R.C. Bilodeau, C.P. Safvan, Dissociative recombination of \(\text{H}_3\text{O}^+\), \(\text{HD}_2\text{O}^+\) and \(\text{D}_3\text{O}^+\), \textit{The Astrophysical Journal} 543, 764-774 (2000).


TUNNELING AND PARITY VIOLATION IN TRISULFANE (HSSSH): AN ALMOST IDEAL MOLECULE FOR DETECTING PARITY VIOLATION IN CHIRAL MOLECULES

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Measuring the parity-violating energy difference $\Delta_{pv}E$ between enantiomers of chiral molecules by spectroscopy is one of the frontiers of highest resolution molecular spectroscopy and a considerable challenge, which so far has not been met with success.[1-5] Over the last decade, considerable progress has been made in the accurate theoretical description of molecular parity violation,[6-8] its possible implications for the origin of molecular chirality and biomolecular homochirality, and its role in the stereomutation dynamics of chiral molecules.[1-5] Accurate theoretical predictions of molecular parity violation importantly assist in a search for the most suitable molecular system. At the same time, tunneling must be studied for candidate molecules, as one must have $\Delta_{pv}E \gg \Delta E_\pm$ (the tunneling splitting for the symmetrical case). In this work we investigate the stereomutation tunneling process in the HSSSH molecule. We report calculations of the parity-violating potential and the ground-state tunneling splitting employing different one- and two-dimensional vibrational Hamiltonians. Our computations utilized the quasi-adiabatic channel reaction path Hamiltonian method,[9] the general rotational-vibrational GENIUSH program package [10] and our recently developed coupled-cluster singles and doubles linear response (CCSD-LR) approach [8] to electroweak quantum chemistry. We report that the ground-state tunneling splitting (for the symmetrical case) is substantially smaller than the parity-violating energy difference. This is the consequence of high interconversion barriers, complex tunneling reaction path and the presence of the three heavy sulphur atoms. Therefore the dynamics of chirality in HSSSH is dominated by de lege symmetry breaking [11] and HSSSH is an ideal candidate for the experiment proposed in [2] to measure $\Delta_{pv}E$, for which the basic experimental capabilities have been demonstrated in our laboratory recently.[12]

References


Absorption lines in the electronic spectra of first row transition metal monohydrides have been recognized in solar and cool stellar spectra. Laboratory work faces a challenge to produce reliable line profiles and positions for their strongest features, illustrated by our recent database\textsuperscript{1} containing line positions and Landé factors for the $F^4\Delta-X^4\Delta$ 0-0 and 1-0 bands of FeH, since stellar temperatures cannot be readily matched in the laboratory, where lower temperatures allow higher (Doppler-limited) resolution. However, to see transitions from levels with low thermal populations, high sensitivity techniques are imperative. We describe here recent work using high sensitivity cw laser techniques (Laser Induced Fluorescence, and Cavity RingDown Spectroscopy), forming the metal hydride radicals in discharge sources.

**NiH**: A CRDS setup, coupling two supermirrors ($R=0.99995$) with a metal hydride discharge source, has been implemented in Lyon and tested by recording absorption coefficients in the weak $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ 0-0 red band of NiH, investigated by O’Brien\textsuperscript{2} using Intracavity Laser Absorption Spectroscopy. The signatures from the minor isotopes of Ni are clearly visible, scanning a cw dye laser to record each line in turn. An important aspect of this work is to optimize radical production, in terms of concentration and stability. Designs based on a coaxial discharge and a sputtering hollow cathode discharge have been tested with the red bands of NiH.

**CrH**: the $A^6\Sigma^+-X^6\Sigma^+$ 0-0 band at 861 nm is a known spectroscopic marker of L-type dwarf stars\textsuperscript{3}, but extensive magnetic response data are currently available only for the ground state. A laboratory survey of both zero-field absolute intensities and magnetic response would help to improve stellar opacity.


models. CrH can be produced with our hollow-cathode sputter source\textsuperscript{4} and we plan to use this in conjunction with the Vernier Frequency Comb spectrometer developed at ILM \textsuperscript{5} for high-sensitivity absorption spectroscopy. The Vernier spectrometer couples a Ti:Sa femtosecond laser to an optical cavity of moderate finesse (300). Its performance as an open cavity is remarkable, covering more than 1300 cm\textsuperscript{-1} in the Ti:Sa emission curve with low baseline noise (baseline 1.7 \texttimes\textsuperscript{8} 10 cm\textsuperscript{-1}); Doppler-limited spectra are recorded in about 1 second.


We have used continuous-wave cavity ring-down spectroscopy to record part of the 2OH excitation range in an Ar/Kr supersonic expansion seeded with H$_2$O. Various bands were observed, and are being rotationally analyzed, of Ar–H$_2$O and Kr–H$_2$O. At present, the analysis of experimental linewidths allowed us to determine the mean upper state predissociation lifetime to be 3 ns for Ar–H$_2$O and 4 ns for Kr–H$_2$O.

In this poster, the latest results concerning Ar–H$_2$O will be highlighted. A band observed at 7275.1 cm$^{-1}$ for this species has been unambiguously assigned to $v_1 = v_3 = 1$, $\Pi(101) \leftarrow \Sigma(000)$, but the dark states perturbing the upper state state have not been assigned, yet, due to the large number of levels of the water monomer near 7250 cm$^{-1}$. In the poster, the results of the analysis will be presented along with the perturbing effects of the dark states. Identification of these will be attempted using a multidimensional approach, based on the intramolecular potential energy surface of Partridge and Schwenke, allowing us to evaluate the rovibrational energy levels of H$_2$O perturbed by the argon atom. Several intermolecular potential will be considered including the one reported by Makarewicz, which assumes a rigid water molecule, and several potentials retrieved in this investigation through $ab$ initio calculations. In these new potentials, the intramolecular coordinates of the water molecule will not be frozen. For each potential, the energy of rotationless states of the Ar–H$_2$O complex will be retrieved up to 7500 cm$^{-1}$ and compared to experimental data.

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UNEXPECTED VAN DER WAALS BANDS IN THE 2OH OVERTONE SPECTRA OF AMMONIA

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We have used continuous-wave cavity ring-down spectroscopy and the FANTA-SIO+ set-up to record part of the 2NH excitation range in an Ar/Kr supersonic expansion seeded with either $^{14}$NH$_3$ or $^{15}$NH$_3$. Various bands were observed, rotationally analyzed and assigned to NH$_3$-Ar/Kr as a carrier$^1$. Unexpected and actually stronger bands were also observed that cannot be assigned to the same carriers. The line spacing for three of these bands looks compatible with that of $^{14}$NH$_3$-Ar$_2$, $^{15}$NH$_3$-Ar$_2$ and $^{14}$NH$_3$-Ar$_3$, the three as predicted from the microwave literature by van Wijngaarden and Jäger$^{2,3}$.

Two more well resolved bands are observed with Kr as a carrier gas seeded with $^{14}$NH$_3$ or $^{15}$NH$_3$ that should then correspond to $^{14}$NH$_3$-Kr$_2$ and $^{15}$NH$_3$-Kr$_2$. Ab initio calculations were performed at the MP2, CCSD(T) and CCSD(T)-F12 levels of theory to predict the unknown rotational constants of $^{14}$NH$_3$-Kr$_2$. These do not match the observed line spacing. These bands, still mysterious at the time of writing this abstract will be presented, as well as the results of the ab initio calculations that were also performed on $^{14}$NH$_3$-Ar$_2$.

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CONVERGENCE AND ISOTOPIC STUDIES OF METHANE SPECTRA BY GLOBAL VARIATIONAL CALCULATIONS

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A detailed convergence study for the methane spectra is presented both for vibrational and rotational degrees of freedom as well as for intensities. Vibration-rotation calculations are carried out using the variational normal mode approach with a full account of the symmetry. The various numerical tests and comparisons in this study suggest that our PES and DMS are currently the most accurate ones in all available observed energy range and that variational calculations are now converged within the error margins of these surfaces. Isotopic effects in methane IR spectra under H→D and 12C→13C substitutions will be also discussed. In Particular, we will focus on the state/polyad and band correspondence for symmetry breaking Td→C3v and Td→C2v substitutions.

This work is supported by French-Russian LIA SAMI and Tomsk State University Mendeleev grant program.

AB INITIO CALCULATION OF ENERGY LEVELS AND RO-VIBRATIONAL SPECTRA FOR SiH₄ MOLECULE

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New potential energy surface (PES) and dipole moment surfaces (DMS) of molecule SiH₄ are constructed using extended ab initio CCSD(T) calculations at 19882 nuclear configurations. The PES and DMS analytical representation are determined through an expansion in symmetry adapted products of internal nonlinear coordinates involving 282 and 692 parameters up to the 8th order and 6th order. Lower vibrational and rovibrational levels are calculated. Good agreement of calculated fundamentals with observed values was found. The integrated intensities of lower polyads was calculated. This work is supported by French-Russian LIA SAMIA. Y. S. CHIZHMAKOVA thanks the Tomsk State University and Academic D.I. Mendeleev Fund Program.

MQDT-ASSISTED HIGH-RESOLUTION SPECTROSCOPY OF THE RYDBERG STATES OF H₂ - IONIZATION ENERGY OF H₂ AND ROVIBRATIONAL STRUCTURE OF H₂⁺

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H₂⁺ and H₂ are the simplest of all molecules and as such are important molecules for the development of molecular quantum mechanics. The rovibrational energy-level structure of H₂⁺ and H₂ can be calculated extremely precisely by quantum chemical methods which include the determination of relativistic and quantum-electrodynamic effects [1,2]. Because the rotational and vibrational transitions of H₂⁺ are electric-dipole forbidden, the experimental data on its energy-level structure are limited.

We present studies of multiphoton transitions to Rydberg states of H₂ belonging to states converging to a wide range of rovibrational levels of H₂⁺ X⁺ (2Σ⁺_g; ν⁺=0-12, N⁺=0-6) at high spectral resolution. By extrapolating the Rydberg series using multichannel quantum-defect theory the vibrational, rotational, fine- and hyperfine-structure intervals of H₂⁺ can be determined precisely [3,4]. The same data can also be used to determine the ionization and dissociation energies of H₂ [5].

Using a home-built pulsed near-infrared laser with Fourier-transform-limited linewidth and adjustable pulse duration, in combination with an improved multiphoton-excitation scheme, we have recently improved the accuracy of these measurements. To this end, systematic errors originating from ac and dc Stark shifts, from pressure shifts, and from the frequency shifts and chirps accompanying the generation of the NIR laser pulses were quantified and minimized.

THE FIRST LABORATORY OBSERVATION OF THE $J = 1 - 0$ ROTATIONAL TRANSITION OF $^{36}\text{ArH}^+$ AND $^{38}\text{ArH}^+$

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Protonated Argon in the $^{36}\text{ArH}^+$ isotopic form has been detected in the Crab Nebula supernova remnant and in the interstellar medium (ISM) through its $J = 1 - 0$ rotational transition at 617.525 GHz. This isotopic species, which has a very low abundance on Earth (0.337 %), is the most abundant in the ISM (84.6 %). The most abundant isotope on Earth, $^{40}\text{Ar}$ (99.6 %), is present only in traces in the ISM (0.025 %). The rotational spectrum of $^{36}\text{ArH}^+$ has never been detected in laboratory so far, despite its remarkable astrophysical importance. In our poster we present the first laboratory observation of the $J = 1 - 0$ transition of $^{36}\text{ArH}^+$ and $^{38}\text{ArH}^+$ (0.063 % abundance on Earth and 15.4 % in the ISM) in natural abundance. The same transition for $^{40}\text{ArH}^+$ and $^{36}\text{ArH}^+$ in the first excited vibrational state $v = 1$ is being investigated.
PREPARATION AND SPECTROSCOPY OF ALKALI-ALKALINE EARTH DIATOMICS ON COLD HELOM DROPLETS

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The unique experimental conditions provided by helium nanodroplets\textsuperscript{1} are utilized to form diatomic molecules from one alkali (Ak) and one alkaline earth (Ake) atom, both heliophobic dopants that reside on the droplet surface. Ak-Ake molecules have attracted considerable attention as candidates for the formation of ultracold molecules with a magnetic and an electronic dipole moment. In order to explore this interesting group of molecules, we measured laser excitation spectra of LiCa\textsuperscript{2}, RbSr\textsuperscript{3,4,5}, and RbCa\textsuperscript{6} on helium droplets. Our own quantum chemistry calculations allowed the assignment of the electronic band systems in the wavenumber range between 11,500 and 23,000 cm\textsuperscript{-1}.

In our studies we found that the permanent electric dipole moment points in different directions for certain electronically excited states, and changes the sign in some cases as a function of bond length. We summarize our results and give possible causes for the measured trends in terms of molecular orbital theory.

Poster Session O

Thursday, August 27, 20:00
The experimental equilibrium structure of acetylene \((\text{C}_2\text{H}_2)\) has been derived by exploiting the highly precise rotational constants \(B_0\) of its 10 isotopologues (containing \(^{12}\text{C}, \, ^{13}\text{C}, \, \text{H}\) and \(\text{D}\)) and the vibration-rotation interaction constants \(\alpha_i^B, \, i = 1,...5\), available in literature.

A fit of all the equilibrium moments of inertia to a two-parameter structure shows a systematic deviation of the residuals and a strong correlation between the \(r_e(\text{CH})\) and \(r_e(\text{CC})\) parameters. Alternative fits are proposed and the possibility of a breakdown of the Born-Oppenheimer approximation is discussed. To date, this work provides the best empirical equilibrium structure of acetylene.
THE INFRARED SPECTRUM OF $^{15}$NH$_3$ IN THE REGION 65-2000 cm$^{-1}$

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The spectra of $^{15}$NH$_3$ were recorded at an unapodized resolution of 0.00096 cm$^{-1}$ in the 65-1200 cm$^{-1}$ range and 0.003 cm$^{-1}$ in the 1200-2000 cm$^{-1}$ region, using the Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beamline, Canadian Light Source, Saskatoon, Canada. The sample pressures were 0.2, 8 and 133 Pa. All the spectra were recorded at 298 K using a multipass coolable absorption cell 2 m base, set for 8 and 72 m path length, with wedged polypropylene windows. The sample was supplied by Sigma-Aldrich with a purity of 98% and used without any further purification.

Rotation-inversion transitions were assigned in the ground state and in the vibrationally excited states $v_2 = 1$, $v_4 = 1$. Ground state transitions were assigned up to $J'' = 22$, including a large number of $\Delta K = 3$ forbidden transitions which allowed the determination of the $K$ dependent spectroscopic parameters $C$, $D_K$, $H_K$ and $L_K$. Rotation-inversion transitions in the $v_3 = 1$, $v_4 = 1$ states were observed and analyzed up to $J' = 20$, $J' = 14$ and $J' = 15$, respectively. A few $\Delta K = 3$ forbidden transitions were also identified in the $v_2 = 1$ state.

A large number of vibration-rotation transitions were assigned to the bands: $v_2$, $v_4$, and $2v_2$, and to the hot bands $2v_2 \leftarrow v_2$, $v_4 \leftarrow v_2$, $2v_2 \leftarrow v_4$. The parameters of the ground state were obtained from a fit of all the transitions assigned in the present work together with all the data reported in the literature and of the ground state combination differences from the analyzed cold bands. All the observed transitions, about 5500, with the exception of those pertaining to the ground state, were analyzed simultaneously on the basis of a model Hamiltonian including all the symmetry allowed interaction terms between and within the excited states, in addition to the vibrational term values and rotation and distortion constants. Most of the transitions were reproduced within their estimated uncertainty. Systematic discrepancies were however observed for $kl = -2$ and $kl = +4$, $J \geq 8$ in the $v_4$ band. The
analysis is still in progress to extend the assignments and to improve the data reproduction.
Fourier transform spectrometers (FTS) based on optical frequency combs (OFC) allow detection of broadband molecular spectra with high signal-to-noise ratios within acquisition times orders of magnitude shorter than traditional FTIRs based on thermal sources \(^1\). Moreover, high absorption sensitivity can be obtained using optical enhancement cavities \(^2\). Due to the pulsed nature of OFCs the interferogram consists of a series of bursts rather than a single burst at zero optical path difference (OPD). The comb mode structure can be resolved by acquiring multiple bursts \(^3\). However, the measurement of molecular lines narrower than the resolution limited by the maximum OPD has not been demonstrated.

We show that it is sufficient to acquire an interferogram in a symmetric range around a single burst with length precisely matched to the comb line spacing in order to exceed the spectrometer’s OPD-limited resolution and measure accurately the intensity change of the individual comb lines. Our method allows measurements of broadband spectra with absorption lines narrower than the OPD-limited resolution without any loss of accuracy due to the instrumental lineshape function. It reduces the acquisition time of high-resolution measurements and interferometer length by orders of magnitude. We demonstrate this by measuring undistorted low pressure CO\(_2\) and CO absorption lines with linewidths narrower than the OPD-limited resolution using OFC-based mechanical FTS in the near- and mid-infrared wavelength ranges \(^4\). The near-infrared system is based on an Er:fiber femtosecond laser locked to a high finesse cavity, while the mid-infrared system is based on a fully-stabilized Tm:fiber-laser-pumped optical parametric oscillator coupled to a multi-pass cell.

The laser induced fluorescence (LIF) spectrum of the $^2\Delta - ^2\Pi$ transition was obtained for SiCN generated by laser ablation under supersonic free jet expansion. The vibrational structure of the dispersed fluorescence (DF) spectra from single vibronic levels (SVL’s) was analyzed with consideration of Renner-Teller (R-T) interaction. Analysis of the pure bending ($\nu_2$) structure by a perturbation approach including R-T, anharmonicity, spin-orbit, and Herzberg-Teller (H-T) interactions indicated considerably different spin splitting for the $\mu$ and $\kappa$ levels of the $^2\Pi$ state of SiCN, in contrast to identical spin splitting for general species based on the usual R-T analysis. Further analysis of the vibrational structure including R-T, anharmonicity, spin-orbit, H-T, Fermi, and Sears interactions was carried out via a direct diagonalization procedure, where the Sears resonance is a second-order interaction combined from spin-orbit and H-T interactions with $\Delta K = \pm 1$, $\Delta \Sigma = \mp 1$, and $\Delta P = 0$. The later analysis reproduced the observed structure, not only the pure $\nu_2$ structure, but also the combination structure of the $\nu_2$ and the Si-CN stretching ($\nu_3$) modes. The analysis demonstrates mixing between vibronic levels, $(01^10) \kappa \Sigma_{\frac{1}{2}}$ and $(02^00) \mu \Pi_{\frac{1}{2}}$, with $\Delta K = \pm 1$ and $\Delta P = 0$, and it is an almost one-to-one mixing giving $|(01^10) \kappa \Sigma_{\frac{1}{2}}\rangle = 0.3|+1;1,-1\rangle + 0.8|+1;2,0\rangle + \cdots$ and $|(02^00) \mu \Pi_{\frac{1}{2}}\rangle = 0.8|+1;1,-1\rangle + 0.3|+1;2,0\rangle + \cdots$, where $|\Lambda;\nu_2,\ell\rangle = |+1;1,-1\rangle$ and $|\Lambda\rangle = |+1;2,0\rangle$ are basis functions of the vibronic Hamiltonian for the numerical diagonalization, and $|\Lambda;\nu_2,\ell\rangle = |\Lambda\rangle|\nu_2,\ell\rangle$ are products between basis functions of electronic, $|\Lambda\rangle$, and two dimensional harmonic oscillator, $|\nu_2,\ell\rangle$. The mixing coefficients of the two vibronic levels agree with those obtained from computational studies\(^\text{2}\). Therefore one may conclude that perturbation treatment alone is inadequate for understanding the vibrational structure of the $^2\Pi$ state of SiCN. For a more complete understanding, it may be necessary to employ numerical diagonalization methods considering Fermi and Sears resonances to describe the vibrational structure.

A QUANTUM CHEMISTRY STUDY OF THE Na₃ GROUND STATE: TUNNELING, FINE AND HYPERFINE STRUCTURE IN A CLASSICAL JAHN-TELLER SYSTEM

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Modern techniques of quantum chemistry allow the prediction of molecular properties to good accuracy, provided the systems are small and their electronic structure is not too complex. For most users of common program packages, ‘chemical accuracy’ in the order of a few kJ/mol for relative energies between different geometries is sufficient. The demands of molecular spectroscopists are typically much more stringent, and often include a detailed topographical survey of multi-dimensional potential energy surfaces with an accuracy in the range of wavenumbers. In a benchmark study of current predictive capabilities we pick the experimentally well studied case of the Na₃ ground state, and present a thorough investigation of the interplay between Jahn-Teller-, spin-orbit-, rovibrational- and hyperfine-interactions based only on ab initio calculations. The necessary parameters for the effective Hamiltonian are derived from the potential energy surface of the 1²E′ ground state and from spin density evaluations at selected geometries, without any fitting adjustments to experimental data. We compare our results to highly resolved microwave spectra.¹

EXPERIMENTAL ROVIBRATIONAL CONSTANTS AND EQUILIBRIUM STRUCTURE OF NITROGEN TRIFLUORIDE

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Several accurate experimental values of the rovibrational interaction constants $\alpha^C$ and $\alpha^B$, the harmonic wave-number parameters $\omega_{ij}$, and the anharmonicity $x_{ij}$ and $g_{ij}$ constants have been extracted from our most recent high-resolution Fourier transform infrared (FTIR), centimeter-wave (CMW) and millimeter-wave (MMW) measurements in the spectra of the oblate symmetric top molecule $^{14}$NF$_3$, contributing thus to the knowledge of the potential of nitrogen trifluoride. The data used are those of the four fundamental, the overtone, the combination and the hot bands identified and analyzed in the range between 400 cm$^{-1}$ and 2000 cm$^{-1}$. Combining the recent experimental values of the constants $\alpha^C$ and $\alpha^B$, with the accurate experimental ground state rotational constants $C_0$ and $B_0$, as for PF$_3$ [1], new equilibrium rotational constants have been evaluated for the pyramidal molecule NF$_3$: $C_e = 0.1968006$ (26) cm$^{-1}$ and $B_e = 0.358981442$ (43) cm$^{-1}$, from which the following equilibrium structure is obtained: $r_e$(F-N) = 1.36757 (58) Å and $\angle_e$(FNF) = 101.8513(10)$^\circ$ [2]. This experimental equilibrium geometry is in excellent agreement with the recent structure determined by ab initio calculations at the CCSD(T)/aug-cc-pVQZ level of theory.

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SYNCHROTRON FTIR SPECTROSCOPY OF CH$_3$SH AT THE CANADIAN LIGHT SOURCE

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The high resolution Fourier transform spectrum of methyl mercaptan has been recorded from 400-1200 cm$^{-1}$ at the Far-Infrared Beamline at the Canadian Light Source in Saskatoon. This region covers the $\nu_8$ C-S stretching band at 710 cm$^{-1}$, the weak $\nu_7$ SH-bending band at 802 cm$^{-1}$ and the strong overlapping $\nu_6$ and $\nu_{11}$ in-plane and out-of-plane CH$_3$-rocking bands at 1072 and 955 cm$^{-1}$, respectively. So far, the C-S stretching band has been extensively analyzed, with $a$-type sub-band assignments for the $v_1=0$ torsional state completed up to $K=12$ for the $A$ symmetry species, $K=10$ for $E_1$ and $K=11$ for $E_2$ up to $J$ values typically above 35. For $v_1=1$, we have identified sub-bands to $K=8$, 7 and 9 for $A$, $E_1$ and $E_2$, respectively, with the exception of the $5E_1$ and $7E_2$ sub-bands which are believed to be strongly perturbed. A number of $v_1=2$ sub-bands have also been assigned for the lower $K$ values.

Analysis has not yet commenced for the higher vibrational modes, but the methyl-rocking bands display remarkably rich and interesting $Q$-branch structure. For the C-S stretching mode, term values have been obtained utilizing ground-state information obtained in our earlier FIR study, \(^1\) and have been fitted to $J(J+1)$ power-series to obtain the substate $J=0$ origins and effective rotational and distortion constants. The origins were then $K$-reduced to isolate the torsional contributions, and the resulting oscillating curves were fitted to a Fourier model as a function of the variable $\rho K$. Shifts of up to 1.5 cm$^{-1}$ are clearly visible for certain levels in the torsional curves, and can be associated with anharmonic coupling to ground-state $v_1=4$ levels that rise up through the C-S stretch region and induce $K$-localized perturbations.

VALIDATION AND EVOLUTION OF THE GEISA SPECTROSCOPIC DATABASE: A NEW APPROACH

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The accuracy of molecular spectroscopy in atmospheric research has entered in a new phase in the frame of remote sensing applications (meteorology, climatology, chemistry) with the advent of highly sophisticated and resolved instrumentations.

The historical background, actual context of management and contents of GEISA (2014 version) are independently presented in a poster by N. Jacquinet et al. In the frame of a necessary new vision for public spectroscopic databases content management, and following the findings of the GEISA workshop¹ (June 2014, Paris, France), we have undertaken a feasibility study on new appropriate methods to bring an added value to GEISA. Besides, one important conclusion of the GEISA workshop was the necessity of a closest feedback between spectroscopy research laboratories and responsible of the management of public spectroscopic databases (such as GEISA and HITRAN), to assess and monitor suitably the archived spectroscopic parameter values traceability and precision.

Based on a strong experience in CAL/VAL activities at LMD, we have developed a chain of validation, aiming to compare the differences between results of model simulations and satellite observations remote data. The simulations are made with the radiative transfer algorithm 4AOP² developed and validated at LMD. In the thermal infrared, instead of laboratory measurements measurements, we have used the richness of the observation data provided by space born satellite instruments like AIRS (2002) and IASI (2006, 2012), TANSO-FTS (2009), CrIs (2011). We are now planning to consider IASI (2017), as well as new generation of higher resolved instruments such as IASI-NG (2021).

In the near infrared, we have used all the potential of one the highest resolved instruments TCCON.

In this poster, we will present results of validations of the GEISA 2014 version, according to IASI and TCCON. Comparisons with other databases like HITRAN 2012 will be given, showing how both databases like HITRAN and GEISA are complementary.

¹GEISA workshop, June 2014, Paris
AB INITIO SPECTROSCOPY FOR TRANSITION METAL DIATOMICS

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Transition metal diatomics such as TiO, VO, TiH and CrH often contribute to the near-IR and visible absorption bands in M-stars and, it is expected, in hot Jupiter exoplanets; for this reason comprehensive spectroscopic line lists for such molecules are important to astronomers, particularly at high temperatures (up to 5000 K). Measurements of transition metal (TM) diatomics are complicated, cover restricted spectral regions and their analysis is challenging because of the high density of lines and presence of perturbations; this complexity is due to the the large number of low-lying and interacting electronic states in these systems. Recorded spectra are traditionally analysed by setting up a model Hamiltonian parametrised by a number of semi-empirical constants, which are then chosen so that they best fit the observed spectrum. Unfortunately fitting constants are often highly correlated, which may lead to erroneous analysis of the physical effects at play and to poor predictive power. For these reasons we believe that an ab initio approach to the spectroscopy of TM diatomics is of critical importance and should be pursued. This route has been considered unfeasible in the past because of the inadequate accuracy of ab initio quantum chemistry methods when applied to TM molecules; while we are still far from achieving spectroscopic accuracy by ab initio means, our approach provides the completeness needed for many low-resolution astrophysical applications; it is also the basis for more physically justified semiempirical models, which should extrapolate better than the traditional ones based on effective Hamiltonians.

We present in our poster the details of our approach, which is based on multi-reference quantum chemistry methods such as complete active space self-consistent field (CASSCF) and multi-reference configuration interaction (MRCI). It is found that MRCI calculations are usually essential for even qualitatively useful results for potential energy and dipole moment curves, while spin-orbit couplings can be reliably computed at the cheaper CASSCF level. We discuss how the choice of the active space affects the accuracy of the curves and comment on the difference of dipole moment curves computed as expectation values (XP) or by way of an energy-derivative (ED) technique; in the case of diagonal dipoles the ED techniques have been demonstrated superior to the
XP one, while for off-diagonal dipole moments the use of the ED technique is problematic.
GLOBAL MODELING OF HIGH-RESOLUTION SPECTRA OF ACETYLENE (C\(_2\)H\(_2\))

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The global modeling of both line positions and intensities of acetylene molecule in the 0-9700 cm\(^{-1}\) region has been performed using the effective operators approach. The parameters of the polyad model of effective Hamiltonian suggested in our paper \(^1\) have been fitted to the line positions collected from the literature. This polyad model of effective Hamiltonian written up to the six-order of perturbation theory takes into account the centrifugal distortion, rotational and vibrational \(\ell\)-doubling terms and both anharmonic and Coriolis resonance interaction operators arising due to the approximate relations between harmonic frequencies: \(\omega_1 \approx \omega_3 \approx 5\omega_4 \approx 5\omega_5; \omega_2 \approx 3\omega_4 \approx 3\omega_5\). The dimensionless weighted standard deviation of the fit is 4.1. The fitted set of 178 effective Hamiltonian parameters allowed reproducing 28000 measured line positions of 325 bands with an RMS value of 0.0035 cm\(^{-1}\). The eigenfunctions of the effective Hamiltonian corresponding to the fitted set of parameters were used to fit the observed line intensities collected from the literature for 10 series of transitions: \(\Delta P=1-10\), where \(P=5V_1+3V_2+5V_3+V_4+V_5\) is the polyad number (\(V_i\) are vibrational quantum numbers). The respective approach is presented in details in our papers \(^2,3\). Using eigenfunctions of a polyad model of global effective Hamiltonian one can describe simultaneously the line intensities of cold and hot bands belonging to the same series of transitions. Our fitted sets of the effective dipole moment parameters reproduce the observed line intensities within their experimental uncertainties. The obtained sets of the effective Hamiltonian and effective dipole moment parameters will be used in the future for the generation of the high temperature spectroscopic data base for acetylene molecule.


ABSORPTION AND EMISSION SPECTRA OF NEUTRAL Au(NHC)X (X=Cl, Br, AND I) AND Au-NHC DOUBLE SALTS CIS/TRANS-[Au(NHC)\textsubscript{2}]\textsuperscript{+}[AuI\textsubscript{2}]\textsuperscript{−}, THEORETICAL STUDY

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Newly synthesized three polymorphic double salts of [Au(NHC)\textsubscript{2}][AuI\textsubscript{2}] (NHC = 1-methyl-3-pyridyl-imidazol-2-ylidene) display interesting photoluminescence properties. The ion pair nature of this Au (I) double salt facilitates the aurophilic interaction and warrants the electronic transition between the [AuI\textsubscript{2}]\textsuperscript{−} centred HOMOs to the Au(NHC)\textsubscript{2}\textsuperscript{+} centred LUMO as supported by DFT calculations. With different Au-Au distances and orientations of the two pyridyl groups, three polymorphs display emissions of green, red, and dual emission of green and red. Conversions among them could be achieved via solvent, vapor, or mechanical stimulations. TD-DFT and DFT calculations are carried out to give insight to the phenomena.
THEORY OF SURFACE-ENHANCED SUM-FREQUENCY GENERATION

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Surface-enhance Raman scattering (SERS) has become a very popular experiment. The surface enhancement of Raman scattering can be attributed to physical enhancement and chemical enhancement. Due to the facts that in SERS the vibrational spectra are often different from Raman spectra but similar to those of resonance Raman spectra, its resonance effect is believed be caused by the surface plasmons or surface states. This type of surface enhancement is studied to see how significant this effect on sum-frequency generation (SFG). The theory of SFG will be developed and compared with surface-enhanced SFG. Quantum chemical calculations of CO/Pt systems are carried out to show the origin of the enhancement.
GLOBAL FREQUENCY AND INTENSITY ANALYSIS OF THE \( \nu_{10}/\nu_7/\nu_4/\nu_{12} \) BANDS SYSTEM OF \( ^{12}\text{C}_2\text{H}_4 \) at 10 \( \mu \)m USING THE \( D_{2h} \) TOP DATA SYSTEM

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A global frequency and intensity analysis of the infrared tetrad located in the 600 – 1500 cm\(^{-1} \) region was carried out using the tensorial formalism developed in Dijon for \( X_2Y_4 \) asymmetric-top molecules\(^1 \) and a program suite called \( D_{2h}TDS \) (now part of the XTDS/SPVIEW spectroscopic software\(^2 \)). It relies on spectroscopic information available in the literature and retrieved from absorption spectra recorded in Brussels using a Bruker IFS 120 to 125 HR upgraded Fourier transform spectrometer, in the frame of either the present or previous work\(^3 \). In particular, 645 and 131 lines intensities have been respectively measured for the weak \( \nu_{10} \) and \( \nu_4 \) bands. Including the Coriolis interactions affecting the upper vibrational levels \( 10^1, 7^1, 4^1 \) and \( 12^1 \), a total of 11632 line positions and 1659 line intensities have been assigned and fitted with global root mean square deviations of \( 3.1 \times 10^{-4} \) cm\(^{-1} \) and 2.4 \%, respectively.

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FREQUENCY AND INTENSITY ANALYSIS OF THE 3 \(\mu m\) REGION OF THE ETHYLENE SPECTRUM USING THE \(D_{2h}\) TOP DATA SYSTEM

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High resolution infrared spectra of the \(\nu_9/\nu_{11}\) region of ethylene, observed from 2900 to 3200 cm\(^{-1}\), have been recorded in Brussels using a Bruker IFS 120 to 125 HR upgraded Fourier transform spectrometer. It is being analyzed following the same line as our previous contribution on the \(\nu_{10}/\nu_7/\nu_4/\nu_{12}\) band system of \(^{12}\)C\(_2\)H\(_4\) at 10 \(\mu m\). We perform a global frequency and intensity analysis using the tensorial formalism developed in Dijon for \(X_2Y_4\) asymmetric-top molecules\(^1\) and a program suite called \(D_{2h}\)TDS (now part of the XTDS/SPVIEW spectroscopic software)\(^2\). A total of 1802 lines have been assigned to the \(\nu_9\) or \(\nu_{11}\) bands. At present, their positions and intensities were fitted with global root mean square deviations of 0.011 cm\(^{-1}\) and 3.5 \%, respectively.

The understanding of the dynamical behavior of functional groups like the amino (NH$_2$) group in biomolecules is essential for a complete understanding of their physical-chemical and biochemical kinetics. In particular, tunneling processes which are generally neglected in classical biomolecular dynamics modeling are in fact important and deserve study. For that reason we have investigated the tunneling dynamics of aniline (C$_6$H$_5$NH$_2$) as a benchmark molecule using high resolution ($\Delta \nu = 17$ MHz) FTIR (THz) spectroscopy with synchrotron radiation. We were able to detect tunneling processes for aniline in the spectral range from 1 to 30 THz (33-1000 cm$^{-1}$). The inversion tunneling dynamics of aniline has been analysed decades ago using low resolution single vibronic level UV fluorescence spectra. We have measured and analysed the inversion tunneling level of aniline at 40.950 31 cm$^{-1}$ and various excited tunneling levels. Numerous interactions have been detected. In particular, we have identified two bands between the two inversion tunneling levels of the first excited inversion state which will be discussed with regard to inversion-torsional splitting. In addition, we have identified the two torsional components rovibrationally resolved due to inversion splitting in the torsional

fundamental of aniline and have detected within each inversion-torsional component two bands.
HIGH RESOLUTION GHz AND THz (FTIR) SPECTROSCOPY AND THEORY OF PARITY VIOLATION AND TUNNELING FOR DITHIINE AS A CANDIDATE FOR MEASURING THE PARITY VIOLATING ENERGY DIFFERENCE BETWEEN ENANTIOMERS OF CHIRAL MOLECULES

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In the framework of ordinary “electromagnetic” quantum theory the ground states of the enantiomers of chiral molecules are energetically equivalent. However, with electroweak quantum chemistry and parity violation, one predicts a small “parity violating” energy difference $\Delta_{PV}E$ on the order of 100 aev, typically, depending on the molecule, corresponding to a reaction enthalpy of stereomutation of about $10^{-11}$ (J/mol)$^{1,2}$. So far, this effect has never been observed experimentally. In our paper, we report exploratory spectroscopy and theory in view of a possible use of the chiral C$_2$-symmetric molecule dithiine (C$_4$H$_4$S$_2$) for detecting molecular parity violation using a current experimental setup in our laboratory$^3$. Using high resolution FTIR spectroscopy$^4$ we were able to provide a first robvibrational analysis of two bands, one centered at 623.3121 cm$^{-1}$ consisting of $\alpha$-type transitions and the second centered at 1308.8724 cm$^{-1}$ consisting of $\alpha$-type transitions. We also report new rotational line frequencies around 100 GHz measured with our frequency locked GHz (submm wave) spectrometer. In parallel, we calculated parity violating potentials using our recent electroweak coupled cluster approach$^5$ and tunneling using our quasidiabatic channel reaction path Hamiltonian approach$^6$.

The implications of our results for the study of molecular parity violation will be discussed.
CO₂ LINE STRENGTHS MEASUREMENTS IN THE 20012–00001 BAND NEAR 2 µm

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The 2 µm band is frequently used for remote CO₂ sensing, e.g., by the Greenhouse Gases Observatory Satellite GOSAT¹ or the Orbiting Carbon Observatory OCO-2². For this purpose, as well as for other applications like future versions of computed or semi-empirical line lists, accurate CO₂ line intensities are essential. The respective 2 µm CO₂ line strength data in HITRAN 2012³ have been measured by Toth et al.⁴. HITRAN 2012 states their uncertainties to be in the 1 to 2 % and 2 to 5 % classes, which is larger than the required uncertainties for the above mentioned remote sensing applications⁴.

We present line strengths measurements of the 100 strongest CO₂ lines in the range from 4850 to 5100 cm⁻¹ (20012–00001 band) using our high-resolution Fourier-Transform Infrared (FTIR) infrastructure developed within the EU-METRISPEC⁵ initiative.

In this work, high-resolution spectra of high purity CO₂ (purity 5.5) were measured with a resolution of 0.002 cm⁻¹ using a Bruker IFS125HR FTIR-spectrometer. In contrast to the commercial versions our spectrometer was evacuated to less than 10⁻⁵ mbar, which ensured a smooth spectral background free of any disturbing H₂O and CO₂ lines usually caused by residual air at some 10⁻² mbar in the spectrometer chamber. CO₂ spectra were measured in a temperature-controlled (296±0.15 K) multi-pass White cell at optical path lengths from 3.2 m to 10 m and CO₂ pressures from 0.1 mbar to 10 mbar. For each spectrum, the total integration time was 10–14 h. Pressure and temperature sensors as well as the gas cell path lengths were calibrated against National Metrology Institutes standards in the full measurement range.

In our contribution, the resulting line strengths are presented and the uncertainties will be discussed. The results are compared to published data, to our

¹Yokomizo M. Greenhouse gases Observing SATellite (GOSAT) ground systems. Fujitsu Sci Tech J (2008);44:410-417
²Thompson DR et al. Atmospheric validation of high accuracy CO₂ absorption coefficients for the OCO-2 mission. J Quant Spectrosc Radiat Transfer (2012);113:2265-2276
⁵www.eumetrispec.eu
own previous laser-based measurements as well as data obtained within the EUMETRISPEC project\textsuperscript{5}.
ULTRAHIGH RESOLUTION MEASUREMENTS OF RO-VIBRATIONAL-TUNNELING TRANSITIONS IN NH₃: ABSOLUTE FREQUENCIES; QUADRUPOLE SPLITTINGS AND A PROOF OF PRINCIPLE EXPERIMENT TO MEASURE MOLECULAR PARITY VIOLATION

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Ammonia has been a prototype molecule for tunnelling for a long time. In the present work we use ammonia as a prototypical test molecule for spectroscopic experiments on molecular parity violation. According to ordinary quantum chemistry including only the electromagnetic interaction the ground state energies of enantiomers of chiral molecules are exactly equal by symmetry. However, this symmetry is broken by the electroweak interaction and a slight energy difference $\Delta_{PV}E$ is introduced between the ground states of the two enantiomers [1-8], the measurement of which is the final goal of our study. The aim of this work is to test both population transfer efficiencies and the ultimate resolution of the setup for the parity violation experiment.

As a test molecule the achiral molecule NH₃ has been chosen. The molecule has large rotational constants and only the lowest rotational levels ($J = 0,1$) are populated in a supersonic molecular beam. The absolute frequencies and quadrupole splittings of the ro-vibrational states of $\nu_1$, $\nu_3^{\pm1}$, $2\nu_4^0$, $2\nu_4^{\pm2}$ have been measured in a pump-probe experiment. A ro-vibrational state has been populated through the absorption of an IR-photon from a continuous wave OPO locked to a frequency comb. In the second step molecules prepared in the excited ro-vibrational level have been probed selectively by a 2+1 REMPI process through the electronically excited B-state ($E''$) or C-state ($A_1'$) [9].

Interaction of titanium dioxide with carbon dioxide has been studied under various circumstances. First, it has been found that TiO$_2$ or other minerals in various forms (anatase and rutile, both synthetic and natural, clays, MgO, FeCO$_3$, CaCO$_3$, basalt) with C$^{18}$O$_2$ undergo spontaneous conversion and C$^{16}$O$_2$ is produced, while the isotopically labeled oxygen is incorporated into the mineral structure. The rate of exchange and the final concentrations depend both on the mineral used (crystalline or amorphous nanoparticles, natural or synthetic) and on a calcination temperature. The mechanism of this reaction is still unknown, but adsorbed water or crystal defects might play a significant role here. Second, it has been found that upon addition of H$^+$ ions, the TiO$_2$ surface becomes activated and CO$_2$ is reduced to CH$_4$. It was generally believed that this is a multistep reaction chain from CO$_2$ via formate, formaldehyde and methanol to CH$_4$, but recently, it has been found, that it is much more complex system of reactions. This reaction depends both on the TiO$_2$ crystalline structure and the presence of H$^+$ ion. Also, minerals such as MgO and FeCO$_3$ exhibit some activity under these very conditions. These reactions point on catalytic abilities of TiO$_2$ and potentially other minerals. Such activity can be both used in modern industry and may help explain atmospheric changes on early Earth, thus pointing toward creation of simple organic molecules and the origins of life itself.

Acknowledgement: The research was supported by the Ministry of Education Youth and Sports of the Czech Republic (COST Action CM1104, contract No. LD14115).
THE GEISA SPECTROSCOPIC DATABASE IN 2014:
CONTEXT AND CONTENTS

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The already important role of molecular spectroscopy in atmospheric research has entered a new promising perspectives phase for remote sensing applications (meteorology, climatology, chemistry) with the advent of highly sophisticated and resolved instrumentations like AIRS (2002), IASI (2006, 2012 and 2017), TANSO-FTS (2009) and CrIs (2011). A precise knowledge of spectroscopic data appear to be at the root of the investigation of climate change providing an improved understanding of the different phenomena driving the atmospheric system.

In this context, the ARA/ABC(t) group at LMD\(^1\) develops and maintains since 1974 - celebrating its 40th birthday during the workshop GEISA\(^2\) (June 2014, Paris, France), the GEISA database (Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information\(^3\)).

GEISA has been at the heart of state-of-the-art developments in spectroscopy and radiative transfer modelling to meet the needs of the international space agencies, by collecting, archiving and distributing all the necessary inputs for atmospheric radiative transfer models. GEISA is constantly evolving, taking into account the best available spectroscopic data. It comprises not only the line-by-line parameters database in the spectral range from 10-6 to 35,877.031 cm\(^{-1}\), but also two additional sub-databases: on infrared and ultraviolet absorption cross-sections and on microphysical and optical properties of atmospheric aerosols. In the frame of the 2014 GEISA last release and of the work in progress in the CNES-MENINGE scientific group for the future of the IASI instruments (IASI-NG), the current contents and planned evolution of each of the GEISA system three sub-databases will be presented.

GEISA and associated management software facilities are implemented on the CNES/CNRS/IPSL Pole Ether scientific centre for research, data, products and distribution services WEB site\(^4\). It is used on-line by more than 300 laboratories working in various domains like atmospheric physics, planetology,

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\(^1\) http://ara.abct.lmd.polytechnique.fr
\(^2\) GEISA workshop, June 2014, Paris
\(^3\) Jacquinet-Husson et al., JQSRT 112, 2395-2445 (2011)
\(^4\) http://ether.ipsl.jussieu.fr/etherTypo/ Ether GEISA website distribution
astronomy, astrophysics. A demonstration of the GEISA access facilities will be made available.
REINVESTIGATION OF THE SECOND TORSIONAL BAND OF METHYLAMINE

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Methylamine is a classic molecule exhibiting two large amplitude motions: CH$_3$ internal rotation and NH$_2$ inversion. These two large amplitude motions are strongly coupled and give rise to a rotation-inversion-torsion structure in the vibrational states. The rovibrational spectrum of the methylamine molecule has been extensively studied both experimentally and theoretically. Previously, the far-infrared spectrum of CH$_3$NH$_2$ in the region of the second torsional excited state, 340-640 cm$^{-1}$, was analyzed by N. Ohashi et al. with resolution of 0.006 cm$^{-1}$. 450 transitions in 13 subbands were assigned. We have restudied the spectrum of methylamine in the 260-720 cm$^{-1}$ region with a resolution of 0.00125 cm$^{-1}$. The spectrum was recorded using Bruker IFS-120HR spectromembrer at the University of Oulu. The work was carried out with the aim of obtaining more detailed information on the second torsional state of methylamine from the analysis of the $\nu = 2 \leftarrow 0$ overtone band spectrum. Because of the broader range of the spectrum complete P, Q and R branches could be observed and the assignments confirmed with the Ground State Combination Differences. Although the line assignments in $\nu = 2 \leftarrow 0$ overtone band spectrum was not straightforward as the spectral lines were strongly overlapped, many transitions, not assigned previously, have been identified. Almost 4000 transitions in 24 subbands of all symmetry species were observed. A global fit has been carried out based on a group theoretical formalism$^2$.

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INFLUENCE OF NANOCONFINEMENT ON ROTATIONAL DEPENDENCE OF LINE HALF-WIDTHS OF CARBON OXIDE

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Absorption spectra of carbon oxide, confined in nanoporous silica aerogel, have been measured within 4100 – 4400 cm$^{-1}$ region at room temperature and at several pressures using Bruker IFS 125 HR Fourier spectrometer. Dependence of the HWHM values on rotational quantum numbers is studied and compared with the data available in literature $^{1,2}$ The half-width values obtained vary from 0.173 to 0.204 cm$^{-1}$, their variations at small quantum numbers are significantly larger than at moderate ones. Line positions are shifted by -0.005 cm$^{-1}$ relative to the lines of free gas. The influence of confinement tightness on rotational dependence and mechanism of formation of spectral line half-widths is discussed.

This work was supported by the Grant of President for young scientists, project MK-7801.2015.2.


ANALYSES OF FOUR BANDS OF THE $^{16}$O$^{18}$O$^{18}$O ISOTOPologue OF OZONE BY CRDS IN THE 5850 – 6920 cm$^{-1}$ REGION

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The very sensitive CW-Cavity Ring Down Spectra of $^{18}$O enriched ozone isotopologues were recorded in the 5850 – 6920 cm$^{-1}$ spectral range$^1$. The ozone generation from two mixtures of $^{16}$O$_2$ and $^{18}$O$_2$ leads to the production of the five $^{18}$O enriched ozone isotopologues, in addition to $^{16}$O$_3$. The contributions of the $^{16}$O$^{16}$O$^{18}$O/$^{16}$O$^{18}$O$^{18}$O and of the $^{16}$O$^{18}$O$^{18}$O/$^{18}$O$^{18}$O$^{16}$O isotopomers were separated using two partial pressures of $^{16}$O$_2$/$^{18}$O$_2$. Here we present the results of the analysis of four rovibrational bands of the $^{16}$O$^{18}$O$^{18}$O isotopologue of $C_S$ symmetry: $7\nu_3$, $2\nu_2 + 5\nu_3$, $2\nu_1 + 2\nu_2 + 3\nu_3$ and $2\nu_1 + 5\nu_3$ centred at 5880, 6055, 6168, 6628 cm$^{-1}$, respectively. The initial assignment was performed using the band centres$^2$ and rotational constants derived from recent theoretical predictions from the molecular potential function$^3$. For each band, the positions and intensities of the assigned transitions were modelled using the effective operator approach. The effective Hamiltonian model includes a number of dark state levels. For each band system, we will present the number of assigned transitions, the statistics of fits and some examples of agreement between measured and simulated spectra.

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FTIR OZONE SPECTRA : FOCUS ON THE $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ C$_{s}$ SYMMETRY ISOTOPIC SPECIES

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Since many years, the GSMA Reims team is working on high resolution IR spectra of the ozone molecule, including isotopic species. The analyses of the C$_{2v}$ ($^{16}\text{O}_3$, $^{18}\text{O}_3$, $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{18}\text{O}$) have been performed in the whole 1000-7900 cm$^{-1}$ domain using either the Reims FT spectrometer, or the Grenoble Cavity Ring Down spectrometer, depending on the spectral range under study.

Here, we will focus our attention on the analyses of the $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ spectra recorded with the FTS of Reims between 800 and 5700 cm$^{-1}$. Thanks to accurate predictions of band centres and rotational parameters, sixteen bands (6986 transitions) have been observed and assigned. We will present parts of the analyses: parameters of the effective Hamiltonian model, number of assigned transitions, statistics of fits and examples of agreement between observed and simulated spectra. We also will present the comparisons between predictions and retrieved of band centres and rotational constants.

In the present contribution we report on the \textit{ab initio} calculations of the sextic centrifugal distortion constants employing anharmonic force fields computed by means of density functional theory (DFT). Different functionals (including the double hybrid B2PLYP) have been employed to calculate cubic force constants and therefore to obtain the corresponding sextic centrifugal distortion constants; the effects related to both the choice of basis sets and the size of integration grid have been evaluated. In this systematic study we present the data for a set of selected molecules of both atmospherical (like halogenated methanes and ethenes) and astrophysical (compounds containing nitrogen and sulphur) relevance that have been used to benchmark the performance of DFT functionals in conjunction to basis sets and integration grids. The predicted values have been compared to both the available data published in literature and those obtained by calculations carried out at MP2 and CCSD level of theory. The obtained results demonstrate that DFT anharmonic force fields can represent a promising reliable and computationally affordable approach to predict sextic centrifugal terms with an accuracy almost comparable to that yielded by the more expensive MP2 and CCSD levels of theory, thus paving the route to the study of more complex systems.
Halocarbon compounds have well known adverse environmental effects and therefore there are many experimental and theoretical studies on their spectroscopic properties. In the present contribution we report on the \textit{ab initio} calculations carried out on 2-chloro-1,1-difluoroethene (R1122) and the comparison with the data coming from spectroscopic investigations carried out both in the microwave and infrared region. Harmonic force fields have been computed at CCSD(T) level of theory employing correlation consistent cc-pVXZ basis sets (X=T,Q,5), thus obtaining the corresponding equilibrium geometries, rotational constants and quartic centrifugal distortion terms. Anharmonic force field calculation up to quartic semidiagonal force constants, performed at CCSD(T)/cc-pVTZ level, yielded anharmonic corrections and the full set of sextic centrifugal distortion terms. By using vibrational perturbation theory to the second order (VPT2), both GVPT2 and HDCPT2 methods were employed to compute the anharmonic corrections to harmonic frequencies. The obtained results have been compared with the available experimental data and those yielded by DFT calculations.
Molecular oxygen $\text{O}_2$ is one of the most important molecules in Earth’s atmosphere. On the other side, the ozone molecule $\text{O}_3$ protects us from the UV radiation when present in the stratosphere, but is very corrosive in the troposphere. The natural abundance in $^{16}\text{O}$ being roughly 99.8%, molecular oxygen and ozone exclusively formed from this isotope are dominant in the atmosphere. Any process happening with these entities is therefore taken as a reference.

Surprisingly, a strong enrichment of about 10% with respect to what happens for $\text{O}_2$, of $\text{O}_3$ in both $^{18}\text{O}$ and $^{17}\text{O}$ species, which seems independent of the isotope mass, and thus known as the so-called mass-independent fractionation (MIF) [1,3], has been observed several decades ago. It has also been reproduced in several laboratory experiments [2]. This phenomenon remains unexplained for the most part and its solution is considered a big challenge within the atmospheric chemistry community.

The three-body recombination $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ is believed to be the main process leading to the isotope enrichment. At low pressures, it can be partitioned into two steps: firstly the formation of $\text{O}_3$ in a highly excited rovibrational state, from reaction $\text{O} + \text{O}_2 \rightarrow \text{O}_3^*$ (step 1), and its subsequent stabilization by deactivation collision with an energy absorbing partner $\text{M}$, $\text{O}_3^* + \text{M} \rightarrow \text{O}_3 + \text{M}$ (step 2). Thus, the efficiency of the exchange reaction $\text{O} + \text{O}_2 \rightarrow \text{O}_3^* \rightarrow \text{O}_2 + \text{O}$, involving $\text{O}_3^*$ as an intermediate, is one of the key parameters to understand ozone formation. We will show that this reaction, initiated by step 1, is very fast with three identical $^{16}\text{O}$ atoms involved, because of a quantum permutation symmetry effect. Consequently, it competes ferociously with step 2 described above, the latter becoming in this way much less effective.

We will present results of a computationally intensive full-quantum investigation of the dynamics [4] of the $^{16}\text{O} + ^{32}\text{O}_2$ supported by a recent accurate global potential energy surface for the ground state of ozone [5]. Our study based on a time independent approach incorporates explicitly the indistinguishability of the three atoms and yields quite accurate cross sections and rate constants. Other results concerning the $^{18}\text{O} + ^{32}\text{O}_2$ exchange reaction will be also presented [6]. Both isotopic and quantum symmetry effects have been
found. Our results will be compared with recent time dependent wave packet results [7,8,9].

LINE PARAMETER CONSISTENCY STUDY OF OZONE AT 4.8 AND 10 µm USING ATMOSPHERIC FTIR SPECTRA FROM THE GROUND

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Atmospheric ozone concentration retrievals from ground or remote sensing mostly depend on spectroscopic parameters that cover different spectral regions. Despite long years of measurement efforts, the uncertainty goal of 1% in absolute line intensities has not been reached yet. Multispectral inter-comparisons using both laboratory and atmospheric studies reveal that important discrepancies exist. We took advantage of the atmospheric spectra recorded with the Bruker 125 Fourier Transform Spectrometer (named FTS-PARIS1) that we operate in the framework of the QualAir air quality station located in downtown Paris on the campus of the Université Pierre et Marie Curie to more closely examine the degree of consistency that can be reached in ozone retrievals using spectral windows in the 5 µm and 10 µm bands of ozone.

In order to obtain an inter-comparison of existing databases, total columns of ozone were retrieved from atmospheric spectra using the spectroscopic parameters available in HITRAN or GEISA and also, to a lesser extent, in S&MPO where the temperature exponent for air-broadening is missing. Data from the 10 µm window are consistent within 0.6% but there are differences when the 5 µm windows are included. The O₃ columns retrieved using the 5 µm windows agree with those obtained in the 10 µm window within 2% but spectroscopic data from HITRAN give about 4% higher results than those from GEISA. This difference may be related to the rescaling of 4% made on the 10µm intensities in the 2004 edition of HITRAN. Furthermore, the sensitivity of the obtained O₃ columns upon the spectroscopic parameters (intensity, lower energy level of the transition, air-broadened line-width and its temperature exponent) has been tested in detail. This work, supported by the french national program LEFE/INSU of CNRS, will be published in the special issue "New Visions of Spectroscopic Databases" of J. Mol. Spectrosc.

HIGH RESOLUTION ANALYSIS OF THE WEAK AND
COMPLEX $\nu_3 + \nu_6 - \nu_4$ AND $\nu_3 + \nu_5$ BANDS OF SF$_6$
MOLECULE: A WAY TO ACCESS $\nu_3 + \nu_6 - \nu_6$ AND $\nu_3 + \nu_5 - \nu_5$
HOT BANDS

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The adequate modeling of the atmospheric absorption of the $\nu_3$ region of SF$_6$
requires to take into account the hot bands $\nu_3+\nu_6-\nu_6$ and $\nu_3+\nu_5-\nu_5$. However
a direct analysis of these hot bands is impossible due to the overlapping of the
structures in this region. Elucidating these hot bands requires therefore the
preliminary studies of other isolated bands including $\nu_3$, $\nu_5$ and $\nu_6$ modes.
In this work, we present an analysis of $\nu_3 + \nu_6 - \nu_4$ providing the $\nu_3 + \nu_6$
parameters to access $\nu_3 + \nu_6 - \nu_6$ and the analysis of $\nu_3 + \nu_5$ to access $\nu_3 + \nu_5 - \nu_5$.
Using the SOLEIL synchrotron facility, and an IFS125HR interferometer
coupled to a cryogenic multiple pass cell $^1$, we could be able to record at high
resolution the $\nu_3 + \nu_6 - \nu_4$ difference band along with other neighboring bands
and the $\nu_3 + \nu_5$ band. The analysis had been performed by using the HTDS
package of the XTDS software developed in Dijon$^2$.

$^1$F. Kwabia Tchana F. Willaert, L. Lago, X. Landsheere, M. Chapuis, P. Roy, and

The electronic ground state of the NCS radical (and, in fact, those of all other 15-valence-electron triatomics such as BO_2, N_2O^+ and NCO) exhibits the Renner effect. At linear geometries, the electronic state is doubly degenerate with \( \Sigma^2 \) symmetry, but it splits into two separate states of \( \Sigma' \oplus \Sigma'' \) symmetries at bent geometries. As a result of the Renner interaction in \( \tilde{X}^2\Sigma \) NCS and of the facts (1) that \( 2\omega_2 \approx \omega_3 \), leading to all-pervading Fermi resonances, and (2) that the spin-orbit coupling constant is close in size to \( \omega_2 \), the resulting rovibronic spectrum is extremely complicated. This spectrum was first observed by Dixon and Ramsay\(^1\) in 1968 with more recent experimental studies from Northrup and Sears,\(^2\) Amano and Amano,\(^3\) and Maeda \(^4\) et al.

Previous theoretical studies of \( \tilde{X}^2\Sigma \) NCS includes the work by Ouazbir \(^5\) et al. These authors calculated \textit{ab initio} the associated rovibronic energies. We extend their work by calculating also rovibronic intensities, thus producing simulated spectra. Our nuclear-motion calculations have been done with the RENNER program system.\(^6\),\(^7\) These calculations are based on new three-dimensional potential energy surfaces and dipole moment surfaces computed \textit{ab initio} at the core-correlated, full-valence MR-SDCI+Q/[aug-cc-pCVQZ(N, C,S)] level of theory. The results obtained are in good agreement with the available experimental data. We hope that the wavenumbers and intensities

predicted for transitions not observed so far will assist in the continued experimental investigation of this molecule.
PRESSURE BROADENING OF THE DIPOLE AND RAMAN LINES OF CO$_2$ BY ARGON: STRINGENT TEST OF CLASSICAL IMPACT THEORY AT DIFFERENT TEMPERATURES

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Classical impact theory of broadening and shift of vibration-rotational spectral lines was proposed in 1966 by Roy G. Gordon [1]. This non-perturbative approach ensures an exact three-dimensional (3D) self-consistent characterization of rotational and translational molecular motions. Brought to revival a decade ago [2], the classical impact theory has acquired a reputation as a very efficient, visual and quite accurate tool. In this work, classical approach is applied to calculate collisional linewidths of CO$_2$ spectral lines perturbed by Ar. Three types of spectra are examined: dipole absorption (000)-(001) band; isotropic and anisotropic Raman Q branches. Simple and elegant formulas of classical impact theory [1] are used along with an exact 3D Hamilton equations for CO$_2$-Ar molecular motion [3]. The calculations utilize Monte Carlo averaging over collision parameters and vibrationally independent most accurate ab initio potential energy surface (PES) of Hutson et al. [4] developed into Legendre polynomial series up to $l_{\text{max}} = 24$. The dependencies of CO$_2$ half-widths on rotational quantum number $J$ up to 100 are computed at temperatures $T = 77, 120, 160, 296, 523, 565, 765$ K and compared with available experimental data as well as with the results of fully quantum CC/CS calculations [5] made with the same PES. To make the picture complete, the predictions of two semi-classical schemes are included, namely, Robert-Bonamy method with isotropic trajectories and improved Smith-Giraud-Cooper formalism [5]. However, these methods demonstrate poor accuracy nearly in all cases. Classical broadening coefficients are in excellent agreement both with measurements and quantum CC/CS results at all nonzero $J$ and at all $T$ (though even at at $J=0$ our classical results are overestimated no more than by 5-8 percents). Summing up, in this work, the evidence of accuracy and efficiency of the classical approach in line broadening calculations is demonstrated once again. Classical impact theory in its present variant is capable to produce quickly and accurately broadening coefficients for any $J$ value (including high J$s$) where other computational methods are either extremely time consuming (like quantum CC/CS) or give erroneous results (like semi-classical methods).

REFERENCES
MICROWAVE SPECTROSCOPY OF NOPINONE-WATER COMPLEXES

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Several monoterpenes and terpenoids are biogenic volatile organic compounds which are emitted in the atmosphere, and react with OH, O₃ and NOₓ etc. to give rise to several oxidation and degradation products. Spectroscopic information on these atmospheric species is still very scarce. Meanwhile we have demonstrated that combining quantum calculations to microwave spectroscopy led to the unambiguous characterization of the most stable conformers for perillaldehyde, limonene, carvone, and nopinone. This information can be used to subsequently model accurately the vibrational signature for atmospheric purposes.

Our work is focused on the rotational spectra of the monohydrates and dihydrates of nopinone, which is one of the major oxidation products of β-pinene. For this task, DFT and ab initio calculations performed at the respectively M06-2X and MP2 levels using the respectively 6-311++G(2df,p) and 6-311++G(d,p) basis set showed that two monohydrates and three dihydrates conformers could be expected.

Using the FTMW spectrometer in Lille, lines of the two monohydrates and of the two most stable dihydrates conformers were found using the predictions made from ab initio calculations. These spectra were recorded in the 2-20 GHz range in a supersonic expansion. Lines were measured and fitted using the Pickett’s program with a semi-rigid rotor Hamiltonian model.

The CaPPA project (Chemical and Physical Properties of the Atmosphere) is funded by the French National Research Agency (ANR) through the PIA (Programme d’Investissement d’Avenir) under contract ANR-10-LABX-005.

HIGH-RESOLUTION INFRARED SPECTROSCOPIC INVESTIGATION OF $^{15}$N-AMMONIA AROUND 1.5 MICRON

T. VANFLETEREN, T. FÖLDES, A. RIZOPOULOS, M. HERMAN, J. VANDER AUWERA, Laboratoire de Chimie quantique et Photophysique, CP160/09, Faculté des Sciences, Université Libre de Bruxelles, 50, ave. Roosevelt, B-1050, Belgium; T.P. SOFTLEY, Department of Chemistry, University of Oxford, Oxford, United Kingdom; G. DI LEONARDO, L. FUSINA, Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, 40136 Bologna, Italy

The FANTASIO experimental set-up coupling a supersonic expansion with a cavity ring-down spectrometer (CRDS) has been used to record jet-cooled spectra of pure $^{15}$NH$_3$ in the $\nu_1 + \nu_3$ range. A room temperature Fourier transform absorption spectrum has also been recorded in the same range to provide reference data. The intensity ratio between the jet-cooled CRDS and room temperature data, as performed with $^{14}$NH$_3$\textsuperscript{1}, will hopefully allow extending the present literature line assignments\textsuperscript{2,3,4}. Absorption from molecular complexes has been observed among monomer lines that will also be compared to $^{14}$NH$_3$ results\textsuperscript{5}.

Invited Lectures P

Friday, August 28, 9:00

Chair: L. ROTHMAN
HIGHLY EXCITED MOLECULAR STATES: CHALLENGE FOR SPECTROSCOPY, DYNAMICS AND ASTROPHYSICS

(45 min.)

V. TYUTEREV, M. REY, T. DELAHAYE†, GSMA, UMR CNRS 7331, Université de Reims, France; A. NIKITIN, S. TASHKUN, R. KOCHANOV‡, LTS, V.E. Zuev Institute of Atmospheric Optics SB RAN Russia; Laboratory QUAMER, Tomsk State University, Tomsk, Russia

Theoretical predictions of excited molecular states and transitions together with extensive rotationally resolved line listes using ab initio potential energy (PES) and dipole moment surfaces have recently become available for small and medium size molecular systems (Refs. 1, 2, 3, 4 and Refs. therein). The high density with the increasing energy makes these calculations challenging but mandatory for analyses of new spectroscopic and dynamics experiments at various temperature and excitation conditions. The state of art in ab initio and empirically optimised surfaces, variational and perturbative calculations from three-to-six atomic molecules (ozone, phosphine, methane, ethylene ... and isotopic species) as well as accuracy and completeness issues will be discussed, particularly for complementary methods currently in progress in Reims and Tomsk groups3, 4, 5, 6, 7, 8, 9, 10. Various applications imply an access to high-energy levels: numerous weak transitions responsible for the opacity in planetary transparency windows at long optical path or an interpretation of high-temperature spectra4 of astrophysical objects. Minimum energy path models9 for the molecular PES, the role of the potential barriers in the transition state channels10 towards the dissociation threshold, the impact of symmetry breaking isotopic substitutions on the resonance coupling and intensity borrowing, qualitative changes of highly excited vibrational modes and perspectives for future studies will be discussed. The work is partly supported by French-Russian LIA SAMIA and Tomsk State University Mendeleev pro-

1X. Huang, D. Schwenke, T. Lee, JCP 134, 044321 (2011)
3M. Rey, A. Nikitin, V. Tyuterev, PCCP 15, 10049 (2013); JMS 291, 85 (2013)
5A. Nikitin, M. Rey, V. Tyuterev, CPL 501, 179 (2011); 565, 5 (2013); JMS 305, 40 (2014)
6V. Tyuterev, S.Tashkun, M. Rey, R. Kochanov, A. Nikitin,T. Delahaye, JPCA 117, 13770 (2013)
7T. Delahaye, A. Nikitin, M. Rey, P. Szalay, V. Tyuterev, JCP 141, 104301(2014).
8M. Rey, A. Nikitin, V. Tyuterev, JCP 141, 044316(2014); JPCA 119, 4763(2015).
9V.Tyuterev, R. Kochanov, S.Tashkun, F. Holka, P.Szalay, JCP 139, 134307 (2013)
gram.

†at present with LISA laboratory, Paris-Creteil, France ‡at present with Harvard-Smithsonian Center for Astrophysics, USA.
ACCURATE SIMULATION OF SPECTRA INVOLVING JT, PJT AND SPIN-ORBIT COUPLING (45 min.)

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Austin, TX USA 78712

The celebrated quasidiabatic Hamiltonian approach of Köppel, Domeke and Cederbaum has been combined with highly-accurate electronic structure calculations, fairly extended parametrizations and approximate diabatization procedures to investigate the electronic spectra of several small molecules. The general computational approach, which involves extensive use of the equation-of-motion coupled-cluster approximation and a related ansatz to derive approximate diabatic states, is discussed and the accuracy of the method is then assessed by looking at some representative examples. These will include various spectra of the NO$_3$ radical (where spin-orbit coupling is not conspicuous) and the photodetachment spectrum of the methoxy and related radicals (where spin-orbit effects are significant).
Poster Session Q

Friday, August 28, 11:00
We present an \textit{ab initio} approach to spectral line-shape modeling and the comparison of the results with experimental data. The most important collisional effects responsible for the formation of the shape of molecular lines are the phase- or state-changing collisions and velocity-changing collisions. Our calculations of these two contributions originate from the interaction potential. We consider the case of molecular hydrogen perturbed by much heavier noble gas atoms (Ar). This system is atypical due to a strong Dicke narrowing and the strong speed dependence of broadening and particularly shifting. It is noteworthy that the first comparison of experimental data and \textit{ab initio} calculations for this system (Raman Q(1) fundamental line) was made 25 years ago and resulted in fundamental discrepancy between the broadenings. Despite several attempts this problem has remained unresolved. We show that this discrepancy is caused by the use of oversimplified description of the model of the velocity-changing collisions\textsuperscript{1}. In our approach, instead of using phenomenological model, we describe the velocity-changing collisions by approximating the $\text{H}_2$-Ar interaction with a hard-sphere potential. The line-shape profile originating from this approach is called speed-dependent billiard ball profile (SDBBP)\textsuperscript{2}. We show, by referring to the collisional kernel derived from \textit{ab initio} classical molecular dynamics simulations, that this approach reproduces the kinetics of the velocity-changing collisions much better than commonly used phenomenological models\textsuperscript{3}. The description of the phase- or


state-changing collisions was determined from quantum close-coupling calculations. Finally, we directly compare our \textit{ab initio} profiles with experimental Raman spectra\cite{1} demonstrating agreement not only for the broadenings, but also for the whole line shapes.

NON-VOIGT LINE-SHAPE ANALYSIS OF H₂ SPECTRA FOR THE HITRAN DATABASE

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Also at: †Institute of Physics, Nicolaus Copernicus University, Grudziadzka 5/7, 87-100 Torun, Poland; ‡Department of Physics and Astronomy, University College London, Gower Street, WC1E6BT London, UK; ††Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, Russia

A proper interpretation and modeling of accurate molecular spectra, at certain pressure/temperature ranges, require the non-Voigt line-shape effects to be incorporated. Therefore, for a more reliable representation of molecular spectra in the HITRAN database, both the Dicke narrowing and speed-dependent effects have to be considered. We demonstrate how to determine and store the line-shape parameters for the case of self-perturbed molecular hydrogen, for which the non-Voigt effects are especially pronounced.

We performed a detailed line-shape analysis of the recent high-quality H₂ spectra recorded with cavity ring-down spectrometers and optical feedback cavity-enhanced absorption spectrometer, showing the possible solutions to the problems of strong numerical correlations between the parameters and their temperature dependences. Note that the previous line-shapes models, which reproduce the H₂ spectra better than the simple phenomenological profiles, are computationally ineffective. Therefore for the purpose of the HITRAN

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database we developed a new technique allowing the Hartmann-Tran profile\(^3\) to be adopted for the H\(_2\) spectra analysis. Finally we demonstrate the use of the new relational structure of the HITRAN database\(^4\) and the HITRAN Application Programming Interface (HAPI)\(^5\) for the case of H\(_2\) spectra.

This work has been supported by NASA Aura Science Team Grant NNX14AI55G and NASA Planetary Atmospheres Grant NNX13AI59G. P.W. is supported by the Foundation for Polish Science TEAM Project co-financed by the EU European Regional Development Fund and by the Fulbright scholarship.


FTIR SPECTRA OF AR I IN 700–7000 cm$^{-1}$ RANGE: HIGH EXCITED (RYDBERG) STATES

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Argon is an inert gas of high importance for both the fundamental physical and astronomical research as well as for many applications (e.g. plasma processing). We present preliminary results of Ar I infrared emission spectra measurement in the 700–7000 cm$^{-1}$ region. Time-resolved Fourier transform infrared spectroscopy with continuous scanning$^1,^2$ was applied to obtain time shifted spectra of pulse discharge with time resolution of 3 $\mu$s and spectral resolution 0.02 cm$^{-1}$. According to our knowledge only sparse experimentally obtained infrared data for Ar I are available in the literature below 1700 cm$^{-1}$. Using the known energy levels and the theoretical predictions of the transition intensities calculated in the quantum defect approximation$^3$ we classified more than 300 emission lines of Ar I.

V.Ch. acknowledges partial support from Russian Ministry of Education & Science (State order no.1122). S.C. acknowledges partial support from the Ministry of Education, Youth and Sports of the Czech Republic (no. LD14115, COST CM1104).

FTIR SPECTRA OF NE I IN 700–7000 cm\(^{-1}\) RANGE: RYDBERG H- AND I-STATES

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EKATERINA M. ZANOZINA, LIBOR JUHA, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Prague 8, Czech Republic; VLADISLAV E. CHERNOV, ANASTASIA A. VORONINA, Voronezh State University, 394693 Voronezh, Russia

Although Ne spectra have been studied from the very beginning of the spectrometric technique development\(^1\), the experimental Ne I spectrum below 1800 cm\(^{-1}\) (wavelengths longer than 5.6 µm) have not been reported yet. We present an extensive laboratory study of Ne I energy transitions in the IR spectral region from 1.43 to 14.0 µm. A big portion of the transitions measured were not observed experimentally before. From the recorded spectra we extract the energies of 6\(h\), 7\(h\) and 7\(i\) levels not reported previously.

The excited energy states of Ne I were produced in a pulsed discharge plasma. A 20 cm long discharge tube with water-cooled stainless steel electrodes was filled with pure neon and during the measurement slow flow of the gas was maintained. The neon pressure was set to 2.1 torr. The voltage drop across the discharge was 0.9 kV, with a pulse width of 22 µs and a peak-to-peak current of 50 mA. The IR spectra of Ne I were recorded using the time-resolved Fourier transform spectrometric method developed in J. Heyrovský UFCH\(^2\). The classification of unknown lines was performed using relative values of the transition intensities calculated in the quantum defect approximation.

V.Ch. acknowledges partial support from Russian Ministry of Education & Science (State order no.1122) S.C. acknowledges partial support from the Ministry of Education, Youth and Sports of the Czech Republic (no. LD14115, COST CM1104).

FORMATION OF FORMAMIDE IN HIGH-ENERGY DENSITY EVENT

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At the end of the 20th century, formamide was proposed to be a parent molecule for nucleic bases during the evolution of life. Though formamide can be a parent molecule, we now show that a key molecule common to all mechanisms of nucleic bases creation is HCN. Since formamide can be regarded as a product of HCN hydrolysis, we do not wish to state that previous assumptions about formamide are wrong. We have measured time-resolved Fourier transform infrared spectra of discharge plasmas of acetonitrile, formamide and methanol in N2/Ar atmosphere. In all acquired spectra we have identified CN radical and also have analyzed final products after the discharge, where formamide was found among other products. These results leads us to the belief that if conditions are plausible, formamide and other much more complicated molecules can be formed from HCN and formamide anywhere in space. And if those mixtures can be found, it is another step towards the unraveling of the creation of life.

Acknowledgement: This work is a part of the research programs funded by the Grant Agency of the Czech Republic (Grant no. 14-12010S).
SPECTROSCOPY OF METEORS AND METEORITES ABLATION PLASMA

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Valašské Meziříčí Observatory, Vsetínská 78, 757 01 Valašské Meziříčí, Czech Republic; E. CHATZITHEODORIDIS, S. GORKOVÁ and
J. KOUKAL, National Technical University of Athens, 9 Heroon Polytechniou str., GR-15780 Zografou, Athens, Greece

The chemical composition of distant objects and events in the universe can be determined using only spectroscopic techniques. To understand the observed spectra, laboratory experiments must be performed to compare the spectral features of individual systems under controlled physical and chemical conditions (individual species concentration, temperature, pressure, and electron density). One plausible experimental approach is to simulate the real conditions using a well-defined system that is easily controlled under laboratory conditions and can be probed using the selected spectroscopic method with sufficient sensitivity (S/N ratio), accuracy, and reproducibility.

Asteroids are remnants from the materials that first formed the planetesimals and planets, and meteorites are pieces of asteroids on Earth that allow us to measure many of the properties of their parent bodies in detail. However, a fundamental problem exists in linking specific meteorites to their parent bodies (primary matter, asteroids, and comet nuclei). The detail description and understanding of their behavior in atmosphere is therefore challenging scientific problem worth of study. When a body enters the Earth’s atmosphere, it is immediately surrounded by meteor plasma and interacts with the highest layers of the Earth’s atmosphere at very high speeds (up to tens of kilometers per second). Descent of a meteoroid through the atmosphere leads to rapid heating, surface ablation and parent body disintegrating. Initial height of meteoroid ablation (early stage of the light, visible part of atmospheric trajectory) depends on geocentric entry speed and initial mass. For known meteor showers (with retrograde orbit, eg. Leonids, Perseids, Orionids), and sporadic meteors with high geocentric velocity, the initial height of ordinary meteors varies between one hundred and one hundred and twenty km. Lowest point of meteoroid visible atmospheric trajectory (end of ablation process) depends besides geocentric speed and initial mass also on zenithal angle of entry into the atmosphere. For meteors with low geocentric velocity and the mass in order of kg may then visible path end height reside between thirty and fifty km above the Earth’s surface. Our target has been a systematization of spectroscopic
emission lines for the comparative analysis of meteor spectra. The solids have been irradiated using excimer laser (Na, Ti, Mg, Al, Si, Fe, and Ca, their simple binary oxides, sulfides, minerals and real sample of meteorites). The discharge plasma in a gas media representing the atmospheres (O\textsubscript{2}, N\textsubscript{2}, Ar, and CO\textsubscript{2}) has been also spectroscopically characterized and used as a buffer gas during the ablation measurement. These spectra have been recorded in situ on the discharges and excimer laser ablations using Fourier time resolved high resolution spectrometer Bruker, high resolution Echelle spectrograph LLA and CCD spectrograph Ocean Optics. Complying data has allowed for not only qualitative determinations of the impacting body composition but also the assignment of spectral lines for products from the meteoroids alterations and plasma interactions in atmosphere.

Acknowledgement: The research has been funded by the Program of regional cooperation of the Czech Academy of Sciences, grant no. R200401521 and by the Program of Origin Action TD1308: Short Term Scientific Missions (STSM).
SO$_2$ - CO$_2$ BROADENING COEFFICIENTS IN THE 9 $\mu$m REGION BY TDL SPECTROSCOPY

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Sulphur dioxide plays a significant role in many fields such as chemistry, biology and industry. It is of interest for the Earth’s atmosphere since it actively enters in the sulphur cycle. The natural sources are biomass burning and volcanic eruptions. The latter are sporadic sources but they can cause huge local fluctuations in the SO$_2$ concentration. The main sources of atmospheric sulphur dioxide arise from anthropogenic activities, being widely used by industry, particularly in food preserving wine making and metallurgy. Once in the atmosphere, it is one of the main causes of acid rains. Sulphur dioxide is also of astrophysical importance: it has been identified in the interstellar medium, in particular in star forming regions, and it has also been detected on the Io surface and in the Venus atmosphere.

With these premises, the collisional line broadening of sulfur dioxide perturbed by carbon dioxide has been investigated for several ro-vibrational transitions within the atmospheric window around 9.1 $\mu$m. The majority of the recorded transitions belong to the $\nu_1$ normal mode, but also lines arising from either the $\nu_1 + \nu_2 - \nu_2$ hot band of the main isotopic species, or the $\nu_1$ band of $^{34}$SO$_2$ have been identified. The measurements have been performed at room temperature by using a tunable diode laser spectrometer equipped with a 92.3 cm path length cell. During the experiments the SO$_2$ pressure has been maintained fixed around 100 Pa, depending on the intensities of the considered lines, and the CO$_2$ pressure has been raised from 350 to 4500 Pa. For each spectral micro-window (about 0.5 cm$^{-1}$ wide) two independent series of measurements have been carried out. The analysis of recorded transitions, performed employing the Voigt model, has led to the determination of the SO$_2$ - CO$_2$ foreign broadening coefficients for about 50 ro-vibrational transitions, with values in the range between 0.08 and 0.14 cm$^{-1}$atm$^{-1}$ and an average value of 0.119(14) cm$^{-1}$atm$^{-1}$. 

VIBRATIONAL ANALYSIS, ABSORPTION CROSS SECTIONS AND QUANTUM CHEMICAL CALCULATIONS OF HFC-152a

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Since their synthesis chlorofluorocarbons (CFCs) found widespread applications mainly as propellants, refrigerants, fire extinguishers, and blowing agents. Nevertheless, their prolonged use contributed to the depletion of the stratospheric ozone layer because they can release Cl radicals which act as a catalyst in ozone-depleting reaction cycles. As a consequence they have been phased out by the Montreal Protocol. As replacement gases, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have been proposed, with the latter option appearing as the most promising one, given the absence of chlorine atoms. Although HFCs do not contribute to the ozone hole, they can behave as greenhouse gases, thus contributing to global warming. For this reason spectroscopic investigations devoted to these molecules should be strongly encouraged. HFC-152a (1,1-difluoroethane, CHF$_2$CH$_3$) represents a potential atmospheric pollutant which has a number of commercial applications, being employed as refrigerant, aerosol propellants and foam expansion agent.

In this contribution, preliminary results about the analysis of the vibrational properties of HFC-152a, performed by adopting an integrated experimental-theoretical approach, are reported. Experimentally, medium resolution spectra have been recorded at room temperature in the far- (FIR) and medium-infrared (MIR) spectral regions by using two different instrumental setups. FIR spectra have been acquired at a resolution of 1 cm$^{-1}$ employing a Nicolet Magna 750 spectrometer equipped with a 16 cm path length cell with polyethylene windows; MIR spectra have been recorded at resolutions of 0.2 and 0.5 cm$^{-1}$ with a Bruker Vertex 70 spectrometer and a 13.4 cm path length cell (KBr windows). In order to determine absorption cross sections, the spectra of CHF$_2$CH$_3$ have also been acquired at different radiator pressures in the range 0.54 - 220 hPa. Theoretically, quantum chemical calculations at CCSD(T) and DFT levels of theory have been carried out in order to support the assignment of the vibrational spectra. Concerning coupled cluster (CC) calculations, the equilibrium geometry and harmonic force fields have been evaluated employing the aug-cc-pV$n$Z ($n = T, Q$) basis set, while for cubic and quartic semi-diagonal force constants the cc-pVTZ basis functions have been employed. Concerning DFT, harmonic and anharmonic calculations
have been carried out at the B2PLYP/cc-pVTZ level. Anharmonic frequencies and coupling terms have obtained from the VPT2 treatment of hybrid CC and CC/DFT force fields. Details of the experimental and computational works will be given and the obtained results, concerning the vibrational analysis (performed in terms of fundamentals, overtones and combination and hot bands) and the determination of absorption cross sections will be presented.
FIRST PRINCIPLES CALCULATION OF ENERGY LEVELS AND SPECTRA FOR AB₄, ABC₃ TYPE MOLECULES

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Molecules of type of AB₄, ABC₃ are interesting both for experimental and theoretical spectroscopy and for intramolecular dynamics. The spectra of ABC₃ molecules could be calculated on a similar manner as AB₄ molecules (like methane ¹ ² ) but specific for these molecules problems have appeared. A big number of PES and DMS parameters requires a much larger number of ab initio points for a robust PES and DMS fit. The big number of parameters could also lead to non-physical behaviour of PES far from equilibrium geometry in the 9D space. A full account of the symmetry properties involve smaller dimensions of basis sets and is benefic for handling strict degeneracies and selection rules, particularly in case of transitions among highly excited vibration-rotation states and high temperatures spectra. Full symmetry variational calculations of vibration-rotation energy levels of symmetric five-atomic molecules CH₃Li, CH₃F (⁴ ⁵), CH₃Cl ⁶, CH₃Br, CH₄ from a PES are discussed. This work is supported by French-Russian LIA SAMIA. B.M. KRISHNA thanks the Tomsk State University and Academic D.I. Mendeleev Fund Program.

ASSIGNMENT AND MODELING OF THE SPECTRUM OF $^{13}$CH$_4$ RECORDED AT 80 K BETWEEN 5853 AND 6200 cm$^{-1}$

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The absorption spectrum of the $^{13}$CH$_4$ methane isotopologue has been recently recorded by Differential Absorption Spectroscopy (DAS) at 80 K in the 5853 – 6200 cm$^{-1}$ spectral range$^1$. This range corresponds to upper part of the tetradecad dominated by the $2\nu_3$ band near 5988 cm$^{-1}$. An empirical list of 3700 lines was constructed from the DAS spectrum.

In this work, we present the first rovibrational assignments obtained using two theoretical approaches: (i) variational calculations$^2$ using ab initio dipole moment surface$^3$ and (ii) calculations based on effective Hamiltonian and effective dipole moment operators. Initial non-empirical effective Hamiltonian for the methane polyads was formed using high-order Contact Transformations (CT)$^4$ from an ab initio PES$^5$.

In total, 2300 lines were assigned to transitions of the tetradecad. Their positions were reproduced with an rms deviation of 5×10$^{-3}$ cm$^{-1}$. About 1300 measured line intensities were modeled using the effective dipole transition moments approach with the rms deviation of about 10%. These new data were used for the simultaneous fit of the $^{13}$CH$_4$ Hamiltonian parameters of the {ground state / dyad / pentad / octad / tetradecad} system and the dipole moment parameters of the {ground state – tetradecad} system.

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VARIATIONAL CALCULATIONS OF THE VIBRATIONAL ENERGIES AND TRANSITION MOMENTS FOR ETHYLENE USING TROVE

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The accurate variational calculations of the ro-vibrational energies for six-atomic molecules is a challenging task, essentially due to the exponentially growing size of the basis set and the increased dimension of the Hamiltonian. The very recent achievements in the large-scale variational calculations are due to Avila and Carrington\textsuperscript{1,2}, who developed very efficient sparse grids for multidimensional quadrature integrations combined with a computationally effective pruning technique for basis sets in the discrete variable representation (DVR). Their results for ethylene molecule served as a benchmark for tests of the MULTIMODE\textsuperscript{3} approach in the two following theoretical studies by Carter et al.\textsuperscript{4,5}.

The approach employed in the present study of ethylene, TROVE\textsuperscript{6}, adopts the product-form Hamiltonian and contracted basis sets in spectral (non-DVR) representation. An overview of a few recent developments in TROVE that effectively obviate the scaling bottleneck for large molecules will be presented. The major idea is the expansion of the Hamiltonian in terms of curvilinear coordinates, rather than normal, and notably the potential\textsuperscript{7}. This leads to a vast reduction in the number of significantly coupled terms in the Hamiltonian and, as a result, considerably advances the basis set convergence. Another idea takes an advantage of the $N$-mode representation of the Hamiltonian in curvilinear coordinates and the structure of the contracted basis set to efficiently evaluate the ro-vibrational matrix elements.

The results of variational calculations will be presented for vibrational energies and transition moments of ethylene, among with a newly calculated \textit{ab initio} potential energy and dipole moment surfaces for this molecule.

This work is supported by the ERC Advanced Investigator Project 267219 and the FP7-MC-IEF project 629237.

\textsuperscript{7}A. Yachmenev and S. N. Yurchenko, \textit{J. Chem. Phys.} (2015), \textit{submitted}.\textsuperscript{7}
DEPERTURBATION ANALYSIS OF THE $A^1\Pi$ STATE IN THE
LESS-ABUNDANT $^{12}\text{C}^{17}\text{O}$ ISOTOPOLOGUE ON THE BASIS
OF INVESTIGATION OF THE $B^1\Sigma^+ \rightarrow A^1\Pi$, $C^1\Sigma^+ \rightarrow A^1\Pi$, $B^1\Sigma^+ \leftarrow X^1\Sigma^+$, AND $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ SYSTEMS

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High-accuracy dispersive optical spectroscopy measurements have been performed on the less-abundant $^{12}\text{C}^{17}\text{O}$ isotopologue observing high resolution emission bands of the $B^1\Sigma^+(v = 0) \rightarrow A^1\Pi(v = 3, 4, \text{and} 5)$ system. These are combined with high-resolution photoabsorption measurements of the $^{12}\text{C}^{17}\text{O}$ $B^1\Sigma^+(v = 0) \leftarrow X^1\Sigma^+(v = 0)$ and $C^1\Sigma^+(v = 0) \leftarrow X^1\Sigma^+(v = 0)$ bands recorded with the VUV-FT spectrometer installed on the DESIRS beamline at the SOLEIL synchrotron. The frequencies of newly observed 401 transitions have been determined in the $15\,180 - 18,400 \text{ cm}^{-1}$ and $86,800 - 87,040 \text{ cm}^{-1}$ regions at absolute accuracy of $0.0015 \text{ cm}^{-1}$ and $0.0060 \text{ cm}^{-1}$ for the strong unblended lines of the $B \rightarrow A$, and $B \leftarrow X,C \leftarrow X$ systems, respectively. Such extended data as well as the previously analysed $(C \rightarrow A)$ transition were used to perform the first deperturbation analysis of the $A^1\Pi$ state in the $^{12}\text{C}^{17}\text{O}$ isotopologue. This analysis included the perturbations in the $A^1\Pi, v = 1 – 5$ rovibrational levels caused by the $I^1\Sigma^-, D^1\Delta, e^3\Sigma^-, a^3\Sigma^+$, and $d^3\Delta$ states. The observed perturbations were compared with those predicted from theoretical calculations.

LASER SPECTROSCOPY OF IRIDIUM MONOCHLORIDE

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Iridium monochloride (IrCl) molecules have been produced in the gas phase using the University of New Brunswick (UNB) laser ablation source. Low resolution laser induced fluorescence (LIF) spectra, obtained using a pulsed dye laser, showed three bands at 557, 545 and 534 nm which appeared to form an upper state vibrational progression. Dispersed fluorescence (DF) spectra, obtained by exciting each band at its band head frequency, showed a ground state vibrational progression extending from \( v = 0 \) to 6. High resolution spectra, taken using a cw ring dye laser, showed resolved rotational structure from both the \(^{193}\text{Ir}^{35}\text{Cl}\) and \(^{191}\text{Ir}^{35}\text{Cl}\) isotopologues. Vibrational assignments of 0-0, 1-0 and 2-0 for the three bands were determined from the isotope structure and the rotational analysis showed the transition to be \(^3\Phi_4 - ^3\Phi_4\), similar to that previously observed in IrF. Doubling of the higher J rotational lines is shown to be caused by quadrupole hyperfine structure. The analysis of the vibrational, rotational and hyperfine structure will be presented.
Emission Spectroscopy of the $B^2\Sigma^- - X^2\Pi$ System of the $^{12}$CD Isotopologue

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The visible spectrum of $^{12}$CD has been investigated at high resolution between 24500 – 27500 cm$^{-1}$ using a high accuracy dispersive optical spectroscopy technique. The CD molecules were produced and excited in a stainless steel hollow-cathode lamp with two anodes and filled with a mixture of He buffer gas and CD$_4$. The emission from the discharge was observed with a plane grating spectrograph and recorded by a photomultiplier tube. The $0-0, 1-0$ and $1-1$ bands of the $B^2\Sigma^- - X^2\Pi$ transition have been measured, while $2-0$ and $2-1$ absorption bands$^1$ have been reanalyzed. The present data were elaborated with help of recent $X^2\Pi$ ground state parameters reported by Zachwieja et al.$^2$ from investigation of the $A^2\Delta - X^2\Pi$ transition. This way the improved spectroscopic constants for the $B^2\Sigma^-$ state of $^{12}$CD have been provided as follows: $\nu_e = 26050.787(11)$ cm$^{-1}$, $\omega_e = 1653.019(25)$ cm$^{-1}$, $\omega_e x_e = 123.899(12)$ cm$^{-1}$, $B_e = 7.08296(32)$ cm$^{-1}$, $\alpha_e = 0.30741(84)$ cm$^{-1}$, and $\gamma_e = -0.10727(42)$ cm$^{-1}$. By using present results the equilibrium parameters for the $B^2\Sigma^-$ states of the CH and $^{13}$CH isotopologues have been improved.

FIRST HIGH RESOLUTION ANALYSIS OF THE \( \nu_{21} \) BAND OF PROPANE AT 921.4 cm\(^{-1}\): EVIDENCE OF LARGE-AMPLITUDE-MOTION TUNNELLING EFFECTS

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A Doppler-limited high resolution (0.0015 cm\(^{-1}\)) spectrum of propane, C\(_3\)H\(_8\), was recorded at 142 K by a Bruker IFS125 Fourier transform spectrometer at SOLEIL, the French synchrotron light source facility. A preliminary analysis of the \( \nu_{21} \) fundamental band (B\(_1\), CH\(_3\) rock) near 921.4 cm\(^{-1}\) reveals that the rotational energy levels of 21\(^1\) are split by interactions with the internal rotations of the methyl groups. Conventional analysis of this A-type band gives band centers at 921.3724(38), 921.3821(33) and 921.3913(44) cm\(^{-1}\) for the AA, EE and AE + EA tunneling splitting components, respectively. \(^1\) These torsional splittings most probably are due to anharmonic and/or Coriolis resonance coupling with nearby highly excited states of both internal rotations of the methyl groups. In addition, several vibrational-rotational resonances were observed that affect the torsional components in different ways. The analysis of the B-type band near 870 cm\(^{-1}\) (\( \nu_8 \), sym. C-C stretch) which also contains split rovibrational transitions due to internal rotation is in progress. It is performed by using the effective rotational Hamiltonian method ERHAM \(^2\) that allows an adequate modeling of such vibration-rotation spectra.

\(^1\)Perrin, Kwabia-Tchana, Flaud, Manceron, Demaison, Vogt, Groner, Lafferty, J. Mol. Spectrosc. (in press)

In this poster we present a possible explanation, based on torsionally mediated proton-spin-overall-rotation interaction operators, for the surprising observation in Nizhny Novgorod several years ago\textsuperscript{1} of doublets in some Lamb-dip sub-millimeter-wave transitions between torsion-rotation states of E symmetry in methanol. These observed doublet splittings, some as large as 70 kHz, were later confirmed by independent Lamb-dip measurements in Kharkov. In this talk we first show the observed J-dependence of the doublet splittings for two b-type Q branches (one from each laboratory), and then focus on our theoretical explanation. The latter involves three topics: (i) group theoretically allowed terms in the spin-rotation Hamiltonian, (ii) matrix elements of these terms between the degenerate components of torsion-rotation E states, calculated using wavefunctions from an earlier global fit of torsion-rotation transitions of methanol in the $v_t = 0$, 1, and 2 states\textsuperscript{2}, and (iii) least-squares fits of coefficients of these terms to about 35 experimentally resolved doublet splittings in the quantum number ranges of $K = -2$ to $+2$, $J = 13$ to 34, and $v_t = 0$. Rather pleasing residuals are obtained for these doublet splittings, and a number of narrow transitions, in which no doublet splitting could be detected, are also in agreement with predictions from the theory. Some remaining disagreements between experiment and the present theoretical explanation will be mentioned.


Sugars are flexible polymorphic species, exhibiting complex constitutional and conformational isomerism. The intramolecular reaction between the carbonyl and one of the hydroxyl groups gives rise to cyclic hemiacetal/ketals, particularly stable for five- (furanose) or six- (pyranose) membered ring forms. A recent microwave spectroscopy study on ribose proved that this aldopentose is a pyranose in gas-phase, with six coexisting low-energy (<6 kJ mol\(^{-1}\)) conformers differing in ring conformation (\(\text{C}_4\) or \(\text{C}_1\)-chairs) and epimerization (\(\alpha/\beta\)).

However, some sugars as ribose, the pyranose form starkly contrasts with the biological preference for five-membered \(\beta\)-ribofuranose rings, most notably in RNA or ATP. In order to explore the molecular structure of a single five-membered ring unit in isolated monosaccharides we studied here \(\beta\)-methyl-D-ribofuranose, using a combination of synthesis, microwave spectroscopy, supersonic jet expansion techniques and laser vaporization methods. Our main objectives include the determination of conformational preferences and number of coexisting species for the free molecule and the comparison with the structural data in condensed phases. The spectrum of \(\beta\)-methyl-D-ribofuranose revealed two conformers that presented hyperfine effects attributed to the internal rotation of the methyl group. In both cases, the methoxy and hydroxymethyl side chains orient themselves to support the presence of intramolecular hydrogens bonds in different ways. Both, the two detected isomers have similar puckering.

ing, which are close to a twisted $^3T_2$ ring conformation. On the other hand, the experimental work was supported by \textit{ab initio} and DFT calculations.
HIGH RESOLUTION SPECTROSCOPY AND QUANTUM DYNAMICS OF FLUOROFORM

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The high resolution spectroscopy of CHF$_3$ has been the basis of the study of time independent and time dependent quantum dynamics for a long time \cite{1, 2, 3, 4, 5, 6, 7, 8, 9}. There have also been substantial efforts concerning the \textit{ab initio} potential hypersurface \cite{10, 11}. We shall present here a survey of some of our recent analyses ranging from the Terahertz (Far infrared) spectral range to about 3000 cm$^{-1}$, with particular emphasis on the pure rotational (FIR) spectra measured at the infrared beamline of the Swiss synchrotron Light Source (SLS), $\nu_3$ fundamental (700 cm$^{-1}$ range), the $\nu_2$, $\nu_5$, $\nu_3 + \nu_6$ polyad (1200 cm$^{-1}$ range), the $\nu_4$, $2\nu_3$ dyad (1400 cm$^{-1}$), the $2\nu_4$ ($A_1$ and $E$) dyad and extensions as available at the time of the conference. The implications for the study of intramolecular vibrational energy redistribution (IVR) will be outlined.

SYNCHROTRON-BASED ROTATIONAL SPECTROSCOPY BETWEEN 0.8 AND 2 THz: ANALYSES OF THE THz SPECTRA OF THE CHIRAL MOLECULES OXIRANE CARBONITRILE (CH$_2$OCHCN) AND METHYL OXIRANE (CH$_2$OCHCH$_3$)

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Chiral precursor molecules of evolution like oxirane carbonitrile$^1$ and other chiral molecules like methyl oxirane are of interest in relation to possible astrophysical observation using spectroscopy$^2,3$. As chiral molecules, the heterocyclic molecule CH$_2$OCHCN (cyanooxirane or in systematic nomenclature oxirane carbonitrile) is also of potential interest when relating biomolecular evolution and molecular parity violation$^4,5,6$.

Using our high resolution FTIR setup at the Swiss Light Source described in Ref.$^7,8$ we have measured the rotational spectra of oxirane carbonitrile and methyl oxirane with a resolution of 18 MHz in the range 1 to 2 THz at room temperature. The analyses will be also discussed with respect to the recent launched THz/FIR telescopes HERSCHEL and SOFIA.

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TWO LINEAR CARBON MOLECULES: AB INITIO POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES OF CCC AND HCCH

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Carbon molecules such as acetylene (C$_2$H$_2$) and C$_3$ are thought to be important sources of opacity in the atmospheres of exoplanets and cool stars. These molecules have been chosen as part of the ExoMol project, aiming to construct a database of theoretically computed hot molecular line lists for species of astrophysical importance. These can be utilised for spectral characterisation of the atmospheres of exoplanets, brown dwarfs and cool stars$^1$.

C$_3$ is of major importance in both combustion and astrophysics. It was first discovered in a cometary spectrum$^2$ and has since been observed in atmospheres of cool carbon stars, supergiant circumstellar shells, and the ISM. Acetylene has also been detected in these environments, along with solar system objects such as Jupiter, Saturn and Titan$^3$.

Accurate potential energy and dipole moment surfaces are required in order to reach this aim, which is the focus here. Linear molecules have to be treated as a special case due to the fact that appropriate coordinates often become undefined at linearity.

An overview will be given of the geometries, basis sets, level of theory and number of grid points used for the computation of ab initio points for the DMS and PES for both these molecules, along with the symmetry adapted analytical functions that were used to represent the ab initio data. Comparisons with previous work will be presented. Ab initio calculations were all performed using MOLPRO. Ro-vibrational energies will be calculated using TROVE$^4$ and DVR3D$^5$ for C$_2$H$_2$ and C$_3$ respectively. Work is being done to implement routines for linear tetratomic molecules into TROVE as standard, this has already been implemented for triatomics.

Other linear carbon molecules already worked on as part of ExoMol project are HCN and HNC$^6$, available at www.exomol.com.

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MOLECULAR LINE LISTS FOR SCANDIUM AND TITANIUM HYDRIDE USING THE DUO PROGRAM

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Transition-metal-containing (TMC) molecules often have very complex electronic spectra because of their large number of low-lying, open-shell, interacting electronic states. The calculation of accurate potential energy curves and couplings is very difficult from the point of view of theory because of the large multi-reference character of the electronic states, the large magnitude of spin-orbit and relativistic effects and the relatively large number of valence electrons and orbitals. As a result of this situation, fully \textit{ab initio} calculations of line positions and intensities of TMC molecules have an accuracy which is considerably worse than the one usually achievable for molecules made up by main-group atoms only. In this poster we report on new theoretical line lists for scandium hydride\textsuperscript{1} ScH and titanium hydride TiH. Scandium and titanium are the lightest transition metal atoms and by virtue of their small number of valence electrons are amenable to high-level electronic-structure treatments and serve as ideal benchmark systems. We report for both systems energy curves, dipole curves and various coupling curves (including spin-orbit) characterising their electronic spectra up to about 20 000 cm\textsuperscript{-1}. Curves were obtained using Internally-Contracted Multi Reference Configuration Interaction (IC-MRCI) as implemented in the quantum chemistry package \textsc{Molpro}. The curves were used for the solution of the coupled-surface ro-vibronic problem using the in-house program \textsc{Duo}\textsuperscript{2}. The resulting line lists for ScH and TiH are made available as part of the \textsc{Exomol} project\textsuperscript{3}.

THE MICROWAVE SPECTRUM OF BENZANILIDE

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Benzanilide(C$_{13}$H$_{11}$NO) is used to produce dyes, pigments and perfumes$^1$. The main characteristic of this molecule is the amide bond, which is ubiquitous in nature.

In contrary to most molecules exhibiting the trans-amide bond, benzanilide shows an unexpected non-planarity. The two resulting symmetry-equivalent conformations are separated by a low energy barrier leading to an internal motion.

The rotational spectra were collected using the Fourier transform microwave spectrometer with a coaxially oriented beam resonator arrangement (COBRA-FT-MW-spectrometer)$^2$. Due to the high melting point of benzanilide the sample was heated to approximately 160°C and was transferred into the gas phase by a super-sonic jet expansion with neon as the carrier gas.

Besides the rotational constants, data obtained from the experimental spectra were the five quartic centrifugal distortion coefficients according to Watson’s S-reduction$^3$ and quadrupole coupling constants using SPCAT/SPFIT$^4$. Furthermore the large amplitude motion of benzanilide could be described by one Coriolis-coupling constant and the difference between the energy levels for the two possible linear combinations for the wave function.

The parameters obtained from the experimental data were compared with calculated parameters using Gaussian 09$^5$.

It appeared that the B3LYP/6-311++G(d,p) among the used methods/basis sets had the highest match with the rotational constants obtained from the experimental spectrum.

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5Gaussian 09, Revision B.01, M.J. Frisch et al., Gaussian Inc., Wallingford CT, 2010
As one of the most abundant family of organic compounds, carboxylic acids are widely used in many fields and have been the subject of numerous studies. Acetic acid is one of the simplest carboxylic acids and may act as excellent models to study the physico-chemical and dynamical properties of acids. In the gas phase, acetic acid is a significant molecule for atmospheric and astro-physical chemistry.

Survey jet-cooled spectra of acetic acid have been recorded in the infrared region (200-4000 cm$^{-1}$) over a wide range of expansion conditions. From the variations of the relative intensities of the signals, vibrational transitions have been assigned unambiguously to the trans-monomer and cyclic-dimer. The IR-active fundamental frequencies have been determined at the instrumental accuracy of 0.5 cm$^{-1}$. This analysis of the jet-cooled spectra supported by electronic structure calculations at the anharmonic level permitted to characterize the trans-monomer/cyclic-dimer equilibrium: from static cell spectra at 298 K, variations of the molar fractions ratio as a function of the total pressure were used to estimate the equilibrium constant and the Gibbs free energy of dimerization at 298 K.

The very good agreement with the literature data shows that the present method is able to produce, from a single study, a free energy value as reliable as the one obtained from a large collection of data. In addition, the semi-empirical free energy value was used to estimate the accuracy of electronic structure calculations and in turn the accuracy of the derived useful information such as the dissociation energy of the complex (i.e. the strength of the hydrogen bonds) or the relative energies within the conformational landscape.1

INTERNAL ROTATION AND QUADRUPOLE COUPLING IN $^{14}$N-METHYLDIACETAMIDE

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Acetyl- and nitrogen containing substances play a very important role in biology and biochemistry. Especially acetamides form a noteworthy class of molecules as they contain a peptide bond, the key element of all peptide molecules and proteins. In this work N-methyldiacetamide ($\text{CH}_3\text{N(COCH}_3\text{)}_2$) was investigated by a combination of molecular beam Fourier transform microwave spectroscopy and quantum chemical calculations.

The title compound contains three methyl groups acting as internal rotors: the methyl group attached to the nitrogen atom (called the $\gamma$-methyl group) and two acetyl methyl groups (called the $\alpha$- and $\beta$-methyl groups). This leads to a rather complicated torsional fine structure. Additionally the spectrum shows quadrupole hyperfine structure due to the $^{14}$N nucleus.

Quantum chemical calculations were carried out at the MP2/6-311++G(d,p) level of theory. By calculating a full potential energy surface with respect to the orientation of both acetyl groups, three stable conformers were found within a range of 35 kJ/mol. Only the lowest energy conformer could be identified under our molecular beam conditions, whereby quadrupole hyperfine and internal rotation splittings due to the $\alpha$- and $\gamma$-methyl group were assigned. No splittings due to the $\beta$-methyl rotor could be resolved, probably because of a high barrier.

The barriers to internal rotation of the $\alpha$- and $\gamma$-methyl rotor were found to be 679.59 cm$^{-1}$ and 147.19 cm$^{-1}$, respectively. These barriers, along with additional internal rotation parameters, the quadrupole coupling constants $\chi_{aa}$ and $\chi_{bb}-\chi_{cc}$, the rotational constants A, B and C and the centrifugal distortion constants could be fitted with very high accuracy. The fit was carried out using the program XIAM with an overall standard deviation of 2.2 kHz, which is close to the experimental accuracy of the spectrometer.
HITRANonline: A New Structure and Interface for HITRAN Line Lists and Cross Sections

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We present HITRANonline, an online interface to the internationally-recognised HITRAN molecular spectroscopic database\(^1\), and describe the structure of its relational database backend\(^2\).

As the amount and complexity of spectroscopic data on molecules used in atmospheric modelling has increased, the existing 160-character, text-based format has become inadequate for its description. For example, line shapes such as the Hartmann-Tran profile\(^3,4\) require up to six parameters for their full description (each with uncertainties and references), data is available on line-broadening by perturbers other than “air” and “self” and more than the current maximum of 10 isotopologues of some molecules (for example, CO\(_2\)) can be important for accurate radiative-transfer modelling. The new relational database structure overcomes all of these limitations as well as allowing for better data provenance through “timestamping” of transitions and a direct link between items of data and their literature sources. Examples of access to data that could not be represented in the old format will be given.

To take full advantage of this new database structure, the online interface HITRANonline, available at hitran.org, provides a user-friendly way to make queries of HITRAN data with the option of returning it in a customizable format with user-defined fields and precisions. Binary formats such as HDF-5 are also supported. In addition to the data, each query also produces its own bibliography (in HTML and BibTeX formats), “README” documentation and interactive graph for easy visualization.


This work has been supported by NASA Aura Science Team Grant NNX14AI55G and NASA Planetary Atmospheres Grant NNX13AI59G.
MICROWAVE SPECTROSCOPIC AND QUANTUM CHEMICAL INVESTIGATIONS ON PHENYL FORMATE AND PHENETOLE

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A pulsed molecular beam Fourier transform microwave spectrometer was used to measure the spectra of phenetole (ethoxybenzene, \( C_6H_5OC_2H_5 \)) and phenyl formate (\( H(CO)OC_6H_5 \)). Theoretical spectra were predicted using the MP2 method in combination with the 6-311G++(d,p) basis set.

For phenetole, a \( C_s \) symmetry was found, and several methods and basis set combinations were applied to check for convergence. In the spectrum, 186 rotational transitions were assigned and fitted to a semi-rigid rotor model with a standard deviation of 2.3 kHz. Highly accurate rotational and centrifugal distortion constants were determined. In agreement with the rather high barriers to internal rotation of the methyl group \( (V_3 = 1174 \text{ cm}^{-1}) \) and the phenyl group \( (V_2 = 626 \text{ cm}^{-1}) \) predicted by quantum chemical calculations, no torsional splittings could be observed.

Initially, we also assumed a \( C_s \) symmetry for the molecular structure of phenyl formate. However, quantum chemical calculations showed that this assumption is not correct. The phenyl ring is tilted out of the \( H(CO)O \) plane, leading to a pair of enantiomers, which can be identified as a double minimum in the calculated potential energy surface (PES). Based on this PES, a simple model calculation indicated a tunneling splitting of approximately 4.5 GHz between the \( 0^+ \) and the \( 0^- \) state. Coriolis interaction between these states affected the rotational transitions and made the spectral assignment difficult.
HIGH RESOLUTION THRESHOLD IONIZATION SPECTROSCOPIC STUDY OF UNSYMMETRICAL CHROMIUM BISARENE COMPLEXES IN A SUPersonic JET

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Together with metallocenes, bisarene complexes play a key role in both fundamental and applied organometallic chemistry. New insights into their electronic structures are provided by the high-resolution methods of REMPI \(^1\), ZEKE \(^2\) and MATI \(^3\) spectroscopy. The symmetric methylated derivatives of bis(benzene)chromium bearing two identical ligands contain several rotational isomers which can be detected in the gas phase by the ZEKE and MATI techniques. The structures of the ZEKE \(^4\) or MATI \(^5\) spectra of individual rotamers are different because of interligand interactions between the substituents. To investigate the ”pure” substituent influence in absence of such effects the unsymmetrical bisarene chromium systems containing one benzene and one methylated benzene ligand have been studied for the first time in this work with the high-resolution MATI technique. The derivatives bearing one, two and three methyl groups as well as (benzene)(biphenyl)chromium were investigated. The spectra of the methylated compounds were compared with those of the corresponding symmetric sandwiches. The precise ionization energies of the neutral species and the vibrational frequencies of the free sandwich ions have been determined. The interpretation of the MATI spectra and analysis of the fine substituent effects were performed on the basis of DFT calculations.

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CONTINUOUS MONITORING OF PHOTOLYSIS PRODUCTS BY TERAHERTZ SPECTROSCOPY

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We demonstrate the potential of THz spectroscopy to monitor the real time evolution of the gas phase concentration of photolysis products and determine the kinetic reaction rate constant. In the primary work, we have chosen to examine the photolysis of formaldehyde (H$_2$CO). Exposure of H$_2$CO to a UVB light (250 to 360 nm) in a single pass of 135 cm length cell leads to decomposition via two mechanisms: the radical channel with production of HCO and the molecular channel with production of CO. A commercial THz source (frequency multiplication chain) operating in the range 600-900 GHz was used to detect and quantify the various chemical species as a function of time. Monitoring the concentrations of CO and H$_2$CO via rotational transitions, allowed the kinetic rate of H$_2$CO consummation to be obtained, and an estimation of the rate constants for both the molecular and radical photolysis mechanisms. We have modified our experimental setup to increase the sensitivity of the spectrometer and changed sample preparation protocol specifically to quantify the HCO concentration. Acetaldehyde was used as the precursor for photolysis by UVC resulting in the decomposition mechanism can be described by:

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \rightarrow CH_4 + CO$$

Frequency modulation of the source and Zeeman modulation is used to achieve the high sensitivity required. Particular attention has been paid to the mercury photosensitization effect that allowed us to increase the HCO production enabling quantification of the monitored radical. We quantify the HCO radical and start a spectroscopic study of the line positions.

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ISOLATED LINE-SHAPE OF METHANE WITH VARIOUS COLLISION PARTNERS

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In this work, we considered the line-shape of methane with various collision partners. The isolated transition P(3) 2A1-3A2 (ν = 1287.813279 cm⁻¹) in the ν₄ band of methane diluted in different perturbers (N₂, O₂, Ar and He) was analysed using different line-shape models, from the simple Voigt profile to the recently recommended Hartmann-Tran profile (HTP)²,³. For each collision-partner, absorption spectra were recorded at room temperature (T = 296 ± 1 K) and at five different pressures (ranging from 29.15 mbar to 95.50 mbar) using a high resolution tunable diode laser spectrometer⁴. Values of spectroscopic parameters for each line-shape model were retrieved using a multi-spectrum fitting procedure. The obtained results confirmed that both of two physical effects, the confinement narrowing⁵ and the speed-dependences of the line broadening and shifting⁶, should be taken into account in order to achieve a better agreement with the experimental data. Among the different considered line-shape models, the HTP led to the best agreement with measured spectra for all considered perturbers.

METALLOCENES AND RELATED TRANSITION METAL CYCLOPENTADIENYL DERIVATIVES

METALLOCENES AND RELATED TRANSITION METAL CYCLOPENTADIENYL DERIVATIVES

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Metalloccenes and related transition metal cyclopentadienyl derivatives represent one of the most intriguing classes of organometallics. Redox parameters appear to play a key role for tuning the chemical reactivity of such sandwich systems and properties of the metallocene-based materials. High resolution data on ionization energies (IEs) of sandwiches are, therefore, of fundamental importance in predicting their chemical behaviour. Among stable metallocenes, only the cobalt complex \(^1\) has been studied so far with the mass-analysed threshold ionization (MATI) technique providing precise IEs of neutral molecules and vibrational frequencies of free ions. Here we report the first photoionization curves and MATI spectra of jet-cooled decamethylmanganocene and (cycloheptatrienyl)(cyclopentadienyl)chromium. The adiabatic ionization potentials of these molecules have been determined to be 43151 and 45243 cm\(^{-1}\), respectively. The vibrational structures of the MATI spectra have been interpreted on the basis of DFT calculations and compared with those of cobaltocene and bis(benzene)chromium \(^2\). Surprisingly, the MATI spectrum of (C\(_7\)H\(_7\))(C\(_5\)H\(_5\))Cr shows much weaker vibronic components as compared to that of isomeric (C\(_6\)H\(_6\))\(_2\)Cr. Decamethylmanganocene represents the first manganese compound revealing higher Rydberg states in the photoionization spectrum.

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GLOBAL ANALYSIS OF HIGH RESOLUTION IR EMISSION SPECTRUM OF $^{12}$CH$_4$ IN THE DYAD ($\nu_2/\nu_4$) REGION

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New experimental high-resolution FTIR emission spectra of methane $^{12}$CH$_4$ have been recently recorded at the SOLEIL synchrotron facility in the so-called Dyad ($\nu_2/\nu_4$) spectral region (1000-1500 cm$^{-1}$) up to about 1400 K under Doppler limited resolution (0.01 cm$^{-1}$). These spectra were fully assigned taking advantage of the STDS global model of methane $^{12}$CH$_4$. This model, which is based on the polyad scheme of the effective Hamiltonian, was developed to deal with all vibration-rotation states of methane up to and including the Tetradecad (6000 cm$^{-1}$) polyad. Thanks to the experimental conditions here, significant improvements have been achieved in this work. The assignments of the well-known cold band (Dyad-GS) and related hot bands up to the Pentad (3000 cm$^{-1}$) are now extended rotationally to $J_{\text{max}} = 30$.

Several thousands of new transitions were assigned for the first time to the high-excited vibration-rotation states of the Octad-Pentad (up to $J = 28$) and the Tetradecad-Octad (up to $J = 21$) hot band system. Assigned line

positions in this work were fitted together with the existing lines using 1120 effective parameters with a dimensionless standard deviation equal to $\sigma = 2.1$. 
FOURIER TRANSFORM SPECTROSCOPY AND GLOBAL DEPERTURBATION ANALYSIS OF THE $A^1\Sigma^+$ AND $b^3\Pi$ STATES IN KRb MOLECULE

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The $A^1\Sigma^+$ and $b^3\Pi$ states of KRb, mixed by strong spin-orbit (SO) interaction, are considered as efficient pathway for Raman transfer production of ultracold molecules in their absolute ground state $X^1\Sigma^+ (v = 0, J = 0)$. In present work we have performed Fourier transform (FT) spectroscopy study and rigorous deperturbation analysis of the A-b complex of KRb similarly as it was realized for KCs and RbCs. The eventual aim was to obtain potential energy curves (PECs) and SO functions, which would allow to reproduce the rovibronic term values with experimental accuracy being about 0.01 cm$^{-1}$. During the experiment A-b→X laser induced fluorescence (LIF) spectra were recorded by FT spectrometer Bruker IFS-125HR. For excitation of the A-b complex either home-made diode lasers or a Ti:Sapphire laser (Coherent MBR-110) were used. The experimental data field contains more than 4000 rovibronic term values of different isotopologues with rotational quantum numbers $J \in [3, 279]$ located in the energy range $[10927, 14250]$ cm$^{-1}$. A direct deperturbation treatment of the experimental term values of $^{39}$K$^{85}$Rb and $^{39}$K$^{87}$Rb isotopologues was accomplished in the framework of coupled-channel (CC) approach. As a result, the 44 mass-invariant fitting parameters of the PECs and SO functions have been required to reproduce 96% of the experimental term values of the A-b complex with a standard deviation of 0.005 cm$^{-1}$. The reliability of the predicted non-adiabatic A-b vibrational wavefunctions was confirmed by a calculation of relative intensity distributions in the A-b→X LIF progressions.

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ROTATIONAL SPECTROSCOPY OF TRANS-METHYLGLYOXAL

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Organic aerosols have a non-negligible effect on atmospheric chemistry, air quality and terrestrial radiation budget. About 90% of the organic aerosols present in urban areas are of secondary type. They are mainly produced in the atmosphere by the oxidation of gaseous precursors.\(^1\) Fu et al.\(^2\) have suggested that trans-methylglyoxal (MG) is a possible precursor of secondary organic aerosols (SOA) in the clouds, its presence in large quantities in the atmosphere being due to the oxidation of specific volatile organic compounds (VOCs).

Upstream from atmospheric studies, the characterization of SOAs precursors by laboratory spectroscopy allows to provide elements for the understanding of the process of formation of these aerosols. For this purpose, we completed the existing pure rotational spectrum of MG in the 6-40 GHz range\(^3\) by new records in a supersonic jet in the 4-20 GHz range (FTMW\(^4\)) and at room temperature in the 150-500 GHz range (mm-/submm-wave spectrometer\(^5\)).

The analysis was made with the support of quantum chemistry calculations (MP2/CBS and B98/CBS using the Gaussian 09 software). The adjustment of the spectroscopic parameters, taking into account the internal rotation related to the presence of a methyl group, was performed using the RAM36 code. The spectra have been reproduced at the experimental precision up to maximal values of J and K\(_a\) equal to 70 and 25, respectively.

The data obtained for the isolated molecule, both experimentally and theoretically, will allow the study of its hydrated complexes and, by comparison, will give access to (micro-)hydration properties. For this purpose, three stable complexes predicted by theoretical calculations will be studied.\(^6\)

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\(^3\) C.E. Dyltick-Brenzinger and A. Bauder, Chem. Phys. 30, 147 (1978)
\(^6\) The CaPPA project (Chemical and Physical Properties of the Atmosphere) is funded by the French National Research Agency (ANR) through the PIA (Programme d’Investissement d’Avenir) under contract ANR-11-LABX-0005-01 and by the Regional Council Nord-Pas de Calais and the European Funds for Regional Economic Development (FEDER).
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The 24th International Conference on High Resolution Molecular Spectroscopy
Prague, Czech Republic, August 30th–September 3rd, 2016

The subjects covered at this meeting are largely identical to those covered at the 24th Colloquium on High Resolution Molecular Spectroscopy. The first circular will be distributed by electronic mail in the fall of 2015.

Information is available from the chairman of the local organizing committee

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