

The **25th** International Conference on

High Resolution Molecular Spectroscopy



Bilbao 2018 September 3rd–7th

Bizkaia Aretoa – UPV/EHU



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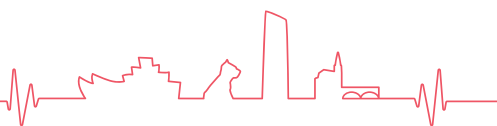
Universidad de Valladolid

The **25th** International Conference on

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Bizkaia Aretoa – UPV/EHU



25th International Conference on High Resolution Molecular Spectroscopy – Abstract Book

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Varios Autores

Bilbao 2018

ISBN: 978-84-09-04373-6

Depósito Legal: BI-1392-2018

Imprime: Grafilur S.L. | www.grafilur.es

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Welcome to the 25th International Conference on High Resolution Molecular Spectroscopy!

It is a pleasure to invite you to the 2018 Edition of the Prague Series of International Conferences on High Resolution Molecular Spectroscopy, to be held in Bilbao (Spain) from September 3rd – 7th, 2018.

Following the tradition of the **Prague Conference Series**, we welcome researchers from around the Globe covering all aspects and varieties of experimental studies, techniques, methods, and theory in high-resolution molecular spectroscopy.

The Bilbao 2018 Conference will be the 25th edition of the Conference, marking the '*Silver Jubilee*' in the meeting's history that started biannually in 1970 to bring together spectroscopists from the East and West of Europe and all around the Globe. Adding to a powerful scientific program with ten invited talks, we will have a commemorative 25th Jubilee Session featuring a lecture by Prof. Dudley R. Herschbach, Nobel Laureate in Chemistry 1986.

The Conference will provide a dynamic forum for scientific discussions, emphasizing on oral pres-

entations. During the preparation of the Conference we have encouraged young researchers to contribute an oral communication. We have accommodated a total of 126 oral communications in three parallel sessions. The most outstanding student talk will be awarded the **Pliva prize 2018**. Additionally, the University of Valladolid will sponsor two additional prizes for oral communications of young researchers. Besides the talks, more than 120 posters in two sessions will complete the conference program. PCCP will sponsor two prizes for poster presentations. Finally, the Dr. Barbara Mez-Starck Foundation will award the International Mez-Starck Prize 2018 at this Conference.

The local organization of the Conference will additionally provide 20 Travel grants for Ph.D. students attending the meeting thanks to the UPV/EHU and the Basque Government.

We are looking forward to welcome you in Bilbao,

Alberto Lesarri, Chair Executive Committee
Emilio J. Cocinero, Chair Local Committee

The **25th International Conference on High Resolution Molecular Spectroscopy** is held under the auspices of the *International Union of Pure and Applied Chemistry* (IUPAC), the *European Association for Chemical and Molecular Sciences* (EuCheMS), the *Atomic and Molecular Physics Division* (GEFAM) and the *Young Chemists Division* (JIQ) of the *Spanish Societies of Physics* (RSEF) and *Chemistry* (RSEQ), the *University of Valladolid*, the *University of the Basque Country* and the *Regional Government of the Basque country*.

The conference is organized jointly by the Department of Physical & Inorganic Chemistry of the *University of Valladolid* (UVa) and the Department of Physical Chemistry of the *University of the Basque Country* (UPV/EHU).

We thank the companies participating or sponsoring the Conference, listed below.

This book contains the schedule of the conference program together with the abstracts of the plenary talks, the 25th anniversary session, oral and poster sessions, along with practical information.

Additional information can be obtained from the Bilbao2018 conference website, the permanent website of the Prague Series of International Conferences, and the dedicated Bilbao2018 mobile app:

Bilbao2018 Conference website:

<http://www.hrms-bilbao2018.com/>

Prague Series Conference website:

<http://www.chem.uni-wuppertal.de/conference/>

Bilbao2018 mobile app: First install "event-sPlace" (from either the Android or the iOS app store), then enter the event "25ichrmsbilbao2018"

For queries during the Conference, please contact the **Technical Secretariat** by email (inscripciones@ercisacongresos.com) or by telephone (+34 94 410 41 77). In case of an emergency, the on-site secretariat can be reached by phone: +34 628 512 803.

**FOR MEDICAL OR POLICE EMERGENCIES CALL
112 IMMEDIATELY!**

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Previous Conferences in the Prague Series:

- 24: PRAHA2016** (August 30–September 3, 2016)
- 23: BOLOGNA2014** (September 2–6, 2014)
- 22: PRAHA2012** (September 4–8, 2012)
- 21: POZNAN2010** (September 7–11, 2010)
- 20: PRAHA2008** (September 2–6, 2008)
- 19: PRAHA2006** (August 29–September 2, 2006)
- 18: PRAHA2004** (September 8–12, 2004)
- 17: PRAHA2002** (September 1–5, 2002)
- 16: PRAHA2000** (September 3–7, 2000)
- 15: PRAHA98** (August 30–September 3, 1998)
- 14: PRAHA96** (September 9–13, 1996)
- 13: Poznań** (September 5–9, 1994)
- 12: Dobříš** (September 7–11, 1992)
- 11: Dobříš** (September 3–7, 1990)
- 10: Liblice** (September 5–9, 1988)
- 9: Liblice** (September 8–12, 1986)
- 8: Liblice** (September 3–7, 1984)
- 7: Liblice** (September 6–10, 1982)
- 6: Liblice** (September 8–12, 1980)
- 5: Liblice** (September 18–22, 1978)
- 4: Liblice** (September 6–10, 1976)
- 3: Liblice** (September 2–6, 1974)
- 2: Prague** (September 4–8, 1972)
- 1: Prague** (June 23–26, 1970)

List of Sponsors

Universidad del País Vasco/ Euskal Herriko Unibertsitatea (UPV/EHU)

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Gobierno Vasco/ Eusko Jaurlaritza (EJ/GV)

Bilbao Ekintza

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European Association for Chemical and Molecular Sciences

Division of Atomic and Molecular Physics of the Spanish Physics and Chemistry Societies (GEFAM)

Young chemical researchers (JIC)

Real Sociedad Española de Química (RSEQ)

Real Sociedad Española de Física (RSEF)

Journal of Molecular Spectroscopy – Elsevier

Springer

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Conference-at-a-glance

Monday, September 3rd	Tuesday, September 4th	Wednesday, September 5th	Thursday, September 6th	Friday, September 7th
08:00–09:45 Registration				
	09:00–9:45 Plenary Lecture 3	09:00–9:45 Plenary Lecture 5	09:00–9:45 Plenary Lecture 7	09:00–9:45 Plenary Lecture 9
09:45–10:30 Opening Ceremony	9:45–10:30 Plenary Lecture 4	9:45–10:30 Plenary Lecture 6	9:45–10:30 Plenary Lecture 8	9:45–10:30 Plenary Lecture 10
10:30–11:10 Coffee Break	10:30–11:00 Coffee Break	10:30–11:00 Coffee Break	10:30–11:00 Coffee Break	10:30–11:00 Coffee Break
11:10 – 11:55 Plenary Lecture 1	11:00–12:40 Oral Sessions	11:00–12:40 Oral Sessions	11:00–12:40 Oral Sessions	11:00–12:40 Oral Sessions
11:55–12:40 Plenary Lecture 2	A3B3C3	A5B5C5	A7B7C7	A9B9C9
13:00 – 14:30 Lunch	13:00 – 14:30 Lunch	13:00 – 14:30 Lunch	13:00 – 14:30 Lunch	13:00 – 14:30 Lunch
14:30–15:50 Oral Sessions	14:30–15:50 Oral Sessions	14:30–15:50 Oral Sessions	14:30–15:50 Oral Sessions	14:30–15:30 Science Salon: Students' Discussion Forum
A1B1C1	A4B4C4	A6B6C6	A8B8C8	
16:00–18:00 Oral Sessions	16:00–18:30 Coffee Break & Poster Session 1	17:00–19:00 XXV Jubilee Session Guggenheim Museum	16:00–18:30 Coffee Break & Poster Session 2	Free afternoon
18:00–20:00 City Hall Reception Bizkaia Aretoa	18:30–20:30 City Tour (Meetig Point: Main Hall, Bizkaia Aretoa)	19:00–20:00 Optional: Guggenheim Museum Visit (reduced fee)	19:00 – 20:00 Boat Tour (Meetig Point: Maritime Museum)	21:00–24:00 Conference Dinner Jauregia Restaurant Euskalduna Concert Hall

BIZKAIA ARETOA

LOCATIONS

Technical Secretariat	Hall		Ground Floor
Plenary Sessions	Mitxelena Room	441 persons	Ground Floor
A Sessions	Mitxelena Room	441 persons	Ground Floor
B Sessions	Baroja Room	161 persons	Second Floor
C Sessions	Oteiza Room	96 persons	First Floor
Poster sessions	Axular Room	Afternoon Coffee Breaks will be there on Tuesday and Thursday	First floor
Poster sessions	Chillida Room	Afternoon Coffee Breaks will be there on Tuesday and Thursday	First floor
Morning Coffee breaks and Sponsors Stands	Hall		Ground Floor
Committee Meeting Room	Barandiarán Room		Ground Floor
Working space	Elhuyar Room		Ground Floor
Meeting space	Laboa Room		Second Floor

Scientific program

Monday, September 3, 2018

Morning Sessions

8:00–9:45	Registration
Main Hall	
9:45–10:30	Opening Ceremony
Mitxelena Auditorium	<p>With the presence of institutions endorsing the conference:</p> <p>Prof. Adolfo Morais Ezquerro Vice Counselor for Research and Universities of the Basque Government</p> <p>Prof. José Luis Martín González Vice Rector for Research of the University of the Basque Country</p> <p>Prof. Fernando Plazaola Muguruza Dean of the Faculty of Science and Technology of the University of the Basque Country</p> <p>Prof. Jens-Uwe Grabow INTERNATIONAL STEERING COMMITTEE Chairman Institut für Physikalische Chemie und Elektrochemie Gottfried Wilhelm Leibniz Universität (LUH)</p> <p>Prof. Alberto Lesarri EXECUTIVE COMMITTEE Department of Physical Chemistry and Inorganic Chemistry Faculty of Sciences University of Valladolid (UVa)</p> <p>Dr. Emilio J. Cocinero LOCAL ORGANIZING COMMITTEE Department of Physical Chemistry Faculty of Science and Technology – University of the Basque Country (UPV / EHU) and Biofisika Institute (CSIC–UPV / EHU)</p>
10:30–11:10	Coffee Break
Main Hall	Sponsors Stands will be placed at Main Hall
	Plenary Session
	Chair: Stepan Urban , <i>University of Chemistry & Technology Prague</i>
11:10–11:55	Plenary Lecture 1
Mitxelena Auditorium	PT1. Collision-induced spectra of N ₂ and O ₂ Ad Van Der Avoird , <i>Radboud University</i>
11:55–12:40	Plenary Lecture 2
Mitxelena Auditorium	PT2. Spectroscopy of molecular radicals in Helium droplets Gary E. Douberly , <i>University of Georgia</i>
13:00–14:30	Lunch Break
	Iberdola tower (black tickets) or Deusto Library (white tickets)

Afternoon Sessions

	Oral Sessions 1		
14:30–15:50	Oral Session A1:	Oral Session B1:	Oral Session C1:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Vadym Ilyushyn , <i>Institute of Radio Astronomy of NASU</i>	Chair: Sonia Melandri , <i>University of Bologna</i>	Chair: Michel Mons , <i>CEA Saclay</i>
	LARGE-AMPLITUDE MOTIONS	WATER CLUSTERS	FREQUENCY COMB AND FAST IR
14:30–14:50	A1.1. Microwave study of internal rotation in para Tolu- aldehyde: local versus global symmetry at the methyl-ro- tor site as an indicator of information transfer across the benzene ring	B1.1. Structures and dynam- ics of acrolein-(H ₂ O) _n clusters revealed by MW spectroscopy and ab initio calculation	C1.1. Fast scanning IR–spec- trometer to measure tran- sient molecules in a pulsed supersonic jet
	Jon Hougen , <i>NIST</i>	Weixing Li , <i>University of Bologna</i>	Daniel Witsch , <i>University of Kassel</i>
14:50–15:10	A1.2. Effective rotational hamiltonian for two-rotor systems with symmetric and asymmetric internal rotors (like Ethanol) applied to Eth- ylphosphine, CH ₃ CH ₂ PH ₂	B1.2. Discovering the confor- mations of formamide com- plexes and formamide–water clusters by microwave spectroscopy	C1.2. Wide bandwidth mid-IR spectroscopy with comb-referenced EC–QCL: application to the ν ₁ funda- mental band of ¹⁴ N ₂ ¹⁶ O
	Peter Groner , <i>University of Missouri – Kansas City</i>	Susana Blanco , <i>Universidad de Valladolid</i>	Davide Gatti , <i>IFN/CNR & Politecnico di Milano</i>
15:10–15:30	A1.3. Proton in a double-well potential: Acetylacetone and its derivatives by microwave spectroscopy	B1.3. Does the structure of the polycyclic aromatic hydrocarbon impact the aggregation of water on its surface? fluorene vs ace- naphthene	C1.3. Endless frequen- cy-swept comb-calibrated spectrometer
	Luca Evangelisti , <i>University of Bologna</i>	Amanda Steber , <i>The Hamburg Centre for Ultrafast Imaging</i>	Thomas Puppe , <i>TOPTICA Photonics AG</i>
15:30–15:50	A1.4. Sensing the molecular structures of alkyl methyl ketones by internal rotation in the microwave spectrum	B1.4. Characterization of microsolvated 15C5 crown ether from broadband rota- tional spectroscopy	C1.4. Broadband complex gas spectroscopy with sub-kHz level resolution comb spec- trometer
	Malke Andresen , <i>IPC RWTH Aachen University</i>	Juan Carlos López , <i>Universidad de Valladolid</i>	Grzegorz Kowzan , <i>Nicolaus Copernicus Univer- sity in Torun</i>

	Oral Session 2		
16:00–18:00	Oral Session A2:	Oral Session B2:	Oral Session C2:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Isabelle Kleiner , <i>LISA / CNRS</i>	Chair: Wen-Bih Tzeng , <i>Academia Sinica</i>	Chair: Donald McNaughton , <i>Monash University</i>
	PES AND SPECTRAL INTERPRETATION	RADICALS AND IONS	SMALL MOLECULES: IR
16:00–16:20	A2.1. Empirical potential energy surface and bending angle probability densities for the electronic ground state of HCO ⁺	B2.1. FTMW spectroscopy of sulfur bearing free radicals, HCSC and CH ₃ SS	C2.1. The water vapor absorption continuum in the atmospheric windows at 4.0, 2.1, 1.6 and 1.25 μm
	Per Jensen , <i>University of Wuppertal</i>	Yasuki Endo , <i>National Chiao Tung University</i>	Alain Campargue , <i>CNRS / Université de Grenoble</i>
16:20–16:40	A2.2. Torsion rotation program for nitromethane CH ₃ NO ₂	B2.2. Millimeter-wave spectroscopy of the HDCCH radical	C2.2. Sub-MHz deuterium spectroscopy and comparison with ab initio calculations of the line-shape effects
	Marek Křęglewski , <i>Adam Mickiewicz University in Poznań</i>	Keiichi Tanaka , <i>Kyushu University</i>	Mikolaj Zaborowski , <i>Nicolaus Copernicus University in Toruń</i>
16:40–17:00	A2.3. Weak intramolecular interaction effects on the structure and torsional spectra of ethylene glycol isotopologues, an astrophysical species	B2.3. Accurate rotational fingerprints of radioactive radicals by mass-independent studies on AlO, TiO, and FeO	C2.3. The high-resolution spectrum of DC ₃ N recorded in the infrared and millimeter-wave regions: a global analysis
	María Luisa Senent , <i>CSIC</i>	Alexander Breier , <i>Universität Kassel</i>	Filippo Tamassia , <i>University of Bologna</i>
17:00–17:20	A2.4. Modelling temperature dependent anharmonic spectra of pyrene (C ₁₆ H ₁₀): comparison of computational approaches	B2.4. Accurate sub-millimeter rest-frequencies for HCCO and DCCO radicals	C2.4. Sub-doppler metrology of HD
	Shubhadip Chakraborty , <i>Institut de Recherche en Astrophysique et Planetologie</i>	Johanna Chantzou , <i>Max Planck Institut for extraterrestrial Physics</i>	Patrick Dupré , <i>Laboratoire de Physico-Chimie de l'Atmosphère</i>
17:20–17:40	A2.5. Non-adiabatic coupling in the ozone molecule	B2.5. Terahertz spectroscopy of isotopologues of amido-gen radical	C2.5. IR laser spectroscopy of the deuterated isotopologues of ammonia
	Alexander Alijah , <i>University of Reims</i>	Mattia Melosso , <i>Università di Bologna</i>	Patrice Cacciani , <i>Université Lille / CNRS</i>
17:40–18:00	A2.6. The long-range behavior of ab initio transition dipole moments and spin-orbit coupling matrix elements between the low-lying electronic states of alkali heterodimers	B2.6. Accurate rotational frequencies of deuterated Ammonium ions (d ₁ -d ₃) measured in a cryogenic ion trap.	C2.6. Photoacoustic spectroscopy of the oxygen a-band in support of OCO-2
	Ekaterina Bormotova , <i>Moscow State University</i>	José Luis Doménech , <i>Instituto de Estructura de la Materia CSIC</i>	Elizabeth Lunney , <i>California Institute of Technology</i>
18:00–20:00 Menchu Gal Terrace	Welcome Cocktail With representatives of the City Council of Bilbao		

Tuesday, September 4, 2018

Morning Sessions

	Plenary Session		
	Chair: Marek Kręglewski , Adam Mickiewicz University in Poznań		
9:00–9:45	Plenary Lecture 3		
Mitxelena Auditorium	PT3. Beryllium bonding probed by anion photodetachment spectroscopy		
	Michael Heaven , Emory University		
9:45–10:30	Plenary Lecture 4		
Mitxelena Auditorium	PT4. Which spectroscopy to study astro-PAHs?		
	Christine Joblin , IRAP – Université de Toulouse		
10:30–11:00	Coffee Break		
Main Hall	Sponsors Stands will be placed at Main Hall		
	Oral Sessions 3		
11:00–12:40	Oral Session A3:	Oral Session B3:	Oral Session C3:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Per Jensen , University of Wuppertal	Chair: José A. Fernández , Universidad País Vasco UPV/EHU	Chair: Robert Gamache , University of Massachusetts Lowell
	LARGE-AMPLITUDE MOTIONS	LIF AND REMPI	INTERMEDIATES, CHIRALITY AND BIOMOLECULES
11:00–11:20	A3.1. Spin–torsion dominated hyperfine splittings in the first excited torsional state ($v_t = 1$) of Methanol	B3.1. High resolution Rydberg spectroscopy of 3d metal sandwich compounds: ultrasensitive probing the electron density changes in organometallic molecules	C3.1. Local interactions of the asparagine and histidine aminoacids in a protein chain: gas phase conformer–selective IR spectroscopy of model molecules
	Li-Hong Xu , University of New Brunswick	Sergey Ketkov , G.A. Razuvaev Institute of Organometallic Chemistry RAS	Michel Mons , CEA Saclay
11:20–11:40	A3.2. Extension of the normal mode approach to nonrigid polyatomic molecules	B3.2. Two-color REMPI $[(1+1)+1]$ of the singlet oxygen $^1\text{O}_2$ arising in UV–photodissociation of van der Waals complex $\text{C}_5\text{H}_8\text{--O}_2$	C3.2. Water sculpts the distinctive shapes and dynamics of the Tn antigens: implications for their molecular recognition
	Dominika Viglaska , University of Reims	Alexandr Bogomolov , Voevodsky Institute of Chemical Kinetics and Combustion	Aran Insausti , Universidad del País Vasco (UPV/EHU)
11:40–12:00	A3.3. Essentially free internal rotation of the Propynyl Methyl group investigated by microwave spectroscopy	B3.3. The vibrational structure of the $\text{NO}_3\text{X } ^2\text{A}_2'$ state studied by SVL DF spectrum	C3.3. Testing the parity symmetry in cold chiral molecules using vibrational spectroscopy
	Konrad Eibl , IPC RWTH Aachen University	Masaru Fukushima , Hiroshima City University	Anne Cournol , Université Sorbonne Paris Cité

12:00–12:20	A3.4. Microwave spectroscopic and quantum chemical studies of the coupled large amplitude motions in S-Phenyl Thioacetate	B3.4. Line shape study of oxygen B-band with CRDS in Dual-Beam configuration	C3.4. Hydrated Lewis antigens in the gas phase: building up the environment or peeling off the solvent?
	Lynn Ferres, <i>IPC RWTH Aachen University</i>	Katarzyna Bielska, <i>Nicolaus Copernicus University in Torun</i>	Pierre Carçabal, <i>Institut des Sciences Moléculaires d'Orsay CNRS</i>
12:20–12:40	A3.5. Separately fitting the torsional symmetry species of molecules with one or multiple internal rotor(s)	B3.5. LIF Spectrum of a $^1\Sigma$ species containing Si: linear SiOSi?	C3.5. High-resolution ro-vibrational spectrum of the simplest Criegee intermediate CH ₂ OO between 880 and 932 cm ⁻¹
	Lam Nguyen, <i>Laboratoire LISA</i>	Masaru Fukushima, <i>Hiroshima City University</i>	Pei-Ling Luo, <i>Institute of Atomic and Molecular Sciences Academia Sinica</i>
13:00–14:30	Lunch Break		
	Iberdrola tower (black tickets) or Deusto Library (white tickets)		

Afternoon Sessions

	Oral Session 4		
14:30–15:50	Oral Session A4:	Oral Session B4:	Oral Session C4:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Filippo Tamassia, <i>University of Bologna</i>	Chair: Leonid Surin, <i>Institute of Spectroscopy RAS</i>	Chair: A. Robert McKellar, <i>National Research Council of Canada</i>
	SMALL MOLECULES: IR	LARGE MOLECULES: MW	LINE SHAPES AND INTENSITIES
14:30–14:50	A4.1. Investigation of the ν_8 and ν_{21} bands of propane CH ₃ CH ₂ CH ₃ at 11.5 and 10.9 μm : evidence of large amplitude tunnelling effects	B4.1. On not yet solved problems concerning some molecular systems investigated by rotational spectroscopy along my research life	C4.1. On the temperature dependence of half-widths and line shifts for molecular transitions in the microwave and infrared regions
	Agnes Perrin, <i>Laboratoire de Meteorologie Dynamique</i>	Walther Caminati, <i>University of Bologna</i>	Robert Gamache, <i>University of Massachusetts Lowell</i>
14:50–15:10	A4.2. High resolution FTIR study of the ν_6 band of CH ₂ F ₂ in 3 μm spectral region at low temperatures	B4.2. Rotational spectrum and molecular structure of succinic anhydride aided by computational calculations	C4.2. Calculation of half widths and line shifts of H ₂ O–N ₂ collision system using the modified complex Robert–Bonamy formalism
	Chilukoti Ashok, <i>Homi Bhabha National Institute</i>	Donald McNaughton, <i>Monash University</i>	Bastien Vispoel, <i>University of Massachusetts Lowell</i>
15:10–15:30	A4.3. The NH ₂ scissors band of Methylamine	B4.3. Pursuing the rotational spectra of large molecular systems	C4.3. High accuracy ab initio DMS and extra high accuracy PES for sub-percent calculation of line intensities
	Iwona Gulaczyk, <i>Adam Mickiewicz University in Poznań</i>	Iker León, <i>Universidad de Valladolid</i>	Oleg Polyansky, <i>UCL</i>

15:30–15:50	A4.4. Wrong distance – wrong line strength – wrong concentrations	B4.4. Exploring the generation of new species using laser ablation Fourier transform microwave spectroscopy techniques: the study of N-carbamoyl glycine	C4.4. Line shape parameters from first principles: investigation of the S and O branches in the H ₂ –He system
	Tom Moses Rubin, <i>PTB</i>	Lucie Kolesníková, <i>Universidad de Valladolid</i>	Hubert Jóźwiak, <i>Nicolaus Copernicus University</i>
16:00–18:30 Axular Room and Chillida Room	Poster Session 1 (P1.1. to P1.63.) and Coffee Break		
18:30–20:30 Meeting point: Main Hall of Bizkaia Aretoa	City Tour		

Poster presentations – Session 1

P1.1. DFT and TD DFT modeling of vibrational structures in high resolution MATI and REMPI spectra of chromium bisarene complexes

Sergey Ketkov; Sheng–Yuan Tzeng; Elena Rychagova; Grigory Zhigulin; Wen–Bih Tzeng

P1.2. Vibronic emission spectroscopy of o–Ethynylbenzyl radical generated from corona discharge of o–Ethynyltoluene

Sang Kuk Lee

P1.3. High resolution study of CH₂=CD₂ molecule: line intensities and half–widths

Kirill Berezkin; Elena Bekhtereva; Olga Gromova; Oleg Ulenikov; Claude Leroy; Christian Sydow; Sigurd Bauerecker

P1.4. The classification of lung cancers and their degree of malignancy by FTIR, PCA–LDA analysis, and a physics–based computational model

Joanna Depciuch; Ewa Kaznowska; Kornelia Łach; Magdalena Kołodziej; Anna Koziorowska; Jitraporn Vongsivut; Izabela Zawlik; Marian Cholewa; Jozef Cebulski

P1.5. Spectroscopy group at the University of the Basque Country

Camilla Calabrese, Aran Insausti; Maider Parra; Cristóbal Pérez; Iciar Uriarte; Imanol Usabiaga; Emilio J. Cocinero; Francisco J. Basterretxea

P1.6. Spectroscopic characterization of the unsaturated Hydrocabons C₃H and C₃H using highly correlated ab initio methods

Maria Luisa Senent; Sara Cherifa Bennedjai; Dalila Hammoutenne

P1.7. Broadening and shifting coefficients of rovibrational lines of HCl perturbed by He in the fundamental and the first overtone regions

Ruslan Asfin; Alexandra V. Domanskaya; Gang Li; Volker Ebert

P1.8. Predissociation of the B state of S₂: measurements and modeling

Glenn Stark; Brenton Lewis; Stephen Gibson; Hannah Herde; Alan Heays; James Lyons; Nelson de Oliveira; Gillian Nave

P1.9. Resonant two–photon ionization and mass–analyzed threshold ionization spectroscopy of 2,4–Difluoroanisole

Wen–Bih Tzeng; Shen–Yuan Tzeng

P1.10. High precision spectrum of the second overtone of ¹²C¹⁶O

Jin Wang; Yu Sun; Anwen Liu; Shuiming Hu

P1.11. CO₂–broadening and shift coefficients in the ν_3 and $\nu_2+(\nu_4+\nu_5)^0$ bands of acetylene

Valerii Perevalov; O.M. Lyulin; T.M. Petrova; A.M. Solodov; A.A. Solodov

P1.12. The ab initio line–shape calculations for purely rotational transitions in the CO–N₂ system

Hubert Jóźwiak; Hubert Cybulski; Franck Thibault; Nikodem Stolarczyk; Piotr Wcisło

P1.13. Spectroscopic study of the $7^1\Pi_u$ and $7^1\Sigma_u^+$ states of Rb₂ molecule

Paweł Kowalczyk; Włodzimierz Jastrzebski; Anna Grochola; Katarzyna Olkowska; Jacek Szczepkowski

P1.14. The $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ absorption spectra at 296 K and 200 K in the range between 6600 and 12000 cm⁻¹

Leonid Sinitsa

P1.15. Study of hydrates of verbenone by microwave Fourier transform spectroscopy and computational chemistry

Pascal Dréan; Mhamad Chrayteh; Annunziata Savoia; Thérèse R. Huet

P1.16. Study of the H₂O–N₂ line broadening and shifting in the region of 16500–17000 cm⁻¹

Leonid Sinitsa; Victor Serdyukov; Nina Lavrentieva; Anna Dudaryonok

P1.17. Rotational–predissociation double resonance spectroscopy of the He–HCO⁺ complex

Oskar Asvany; Thomas Salomon; Matthias Töpfer; Phillip Schreier; Stephan Schlemmer; Hiroshi Kohguchi; Leonid Surin

P1.18. Combined PGOPHER analysis of bands in the 1st positive system of N₂, 4500 – 15500 cm⁻¹

Amanda Ross; Patrick Crozet; Jérôme Morville; Colin Western; Dennis Tokaryk

P1.19. Properties of HF@C₆₀ endofullerene from first principles

Yulia Kalugina; Pierre–Nicholas Roy

P1.20. High sensitivity Cavity Ring Down Spectroscopy spectroscopy of the $\nu_1+4\nu_3$ band of NO₂ near 1.34 μm

Anastasiia Lukashevskaya; Didier Mondelain; Alain Campargue; Valerii Perevalov

P1.21. Laser absorption spectroscopy of methane at 1000 K between 1.75 and 1.3 μm

Alain Campargue; Semyon Vasilchenko; Mélanie Ghysels; Didier Mondelain; Samir Kassi; Solenne Barry

P1.22. Double resonance rotational spectroscopy of CH₃⁺ – He

Matthias Töpfer; Thomas Salomon; Stephan Schlemmer; Oskar Asvany; Otto Dopfer; Hiroshi Kohguchi; Koichi M. T.

P1.23. The absorption band of nitrogen dioxide ($^{14}\text{N}^{16}\text{O}_2$) by CRDS near 6000 cm⁻¹

Anastasiia Lukashevskaya; Olga Naumenko;; Samir Kassi; Alain Campargue

P1.24. Isolated small–amplitude fundamental embedded in a pure torsional bath: assignment and fit of the FIR and microwave spectra of the ν_{10} vibrational state of acetaldehyde

Vadym Ilyushyn; Eugene Alekseev; Olga Dorovskaya; Laurent Margulès; Roman Motiyenko; Manuel Goubet; Olivier Pirali; Sigurd Bauerecker; Christof Maul; Christian Sydow; Georg Mellau; Isabelle Kleiner; Jon T. Hougen

P1.25. The high resolution spectrum of $^{14}\text{ND}_3$ in the far–infrared

Elisabetta Cane; Gianfranco Di Lonardo; Luciano Fusina; Adriana Predoi–Cross; Filippo Tamassia

P1.26. Line positions and intensities for the ν_3 band of 5 isotopologues of germane for planetary applications

Vincent Boudon; Tigran Grigoryan; Florian Philipot; Fridolin Kwabia Tchana; Laurent Manceron; Athéna Rizopoulos; Jean Vander Auwera; Thérèse Encrenaz

P1.27. The third and fourth torsional states of acetic acid

Vadym Ilyushyn; Olga Dorovskaya; Eugene Alekseev

P1.28. First detection of H₂³⁶S in the infrared region

Valeriya A. Zamotaeva; Elena S. Bekhtereva; Olga V. Gromova; Oleg N. Ulenikov; Claude Leroy; Christian Sydow; Sigurd Bauerecker

P1.29. New electronic states in the spectra of TaH and TaD

Thomas Varberg; Samuel Gleason; Dalir Kellett; Paul Reischmann

P1.30. Accurate first principles global calculations and isotopic effects on infrared spectra for phosphine PH₃ and hydrocarbons (CH₄, C₂H₄)

Vladimir Tyuterev; Dominika Viglaska; Michael Rey; Andrey Nikitin; Eveniya Starikova

P1.31. Vibrational dependence and prediction of line shape parameters for the H₂O–H₂ collisional system

Robert Gamache; Bastien Vispoel

P1.32. Ab initio reduced matrix elements for H₂¹⁶O: application to H₂O–H₂ line shape calculations via the modified complex Robert–Bonamy method

Bastien Vispoel; Robert Gamache

P1.33. Classical trajectory simulation of collision-induced absorption spectra

Daniil N. Chistikov; Artem A. Finenko; Yulia N. Kalugina; Sergei E. Lokshtanov; Sergey V. Petrov; Andrey A. Vigasin

P1.34. Atlas of experimental and theoretical high-temperature methane cross-sections from T=296 K to 1000 K in the mid-infrared range

Vladimir Tyuterev; Andy Wong; Peter Bernath; Michael Rey; Andrey Nikitin

P1.35. High-resolution laser spectroscopy of nitrogen dioxide in the region of 14500–16800 cm⁻¹

Shunji Kasahara; Takumi Yoshizawa; Michihiro Hirata; Kohei Tada

P1.36. Modified complex Robert–Bonamy calculations including line coupling on the H₂O–N₂ and CO₂–N₂ molecular systems

Bastien Vispoel; Richard Lynch; Robert Gamache

P1.37. Temperature dependence of line broadening coefficient of chloromethane diluted in carbon dioxide

Sylvain Léonis; Muriel Lepere

P1.38. A room-temperature HCN line list with a new dipole moment surface

Vladimir Makhnev; Aleksandra Kyuberis; Oleg Polyansky; Irina Mizus; Jonathan Tennyson; Nikolay Zobov

P1.39. Quantum chemical characterisation of difluorine peroxide FOOF

Olfa Ferchichi

P1.40. On the consistency of absolute ozone intensities in MW, 10 and 5 micron ranges from ab initio predictions and laboratory observations

Vladimir Tyuterev; Alain Barbe; Semen Mikhailenko; Evgeniya Starikova

P1.41. Rotational and vibrational dependences of line half-widths for CO confined in silica aerogel

Alexander A. Solodov; Tatyana M. Petrova; Yuriy N. Ponomarev; Alexander M. Solodov

P1.42. Measurements and calculations of H₂– broadening and shift parameters of water vapor transitions in 6700–9000 cm⁻¹ spectral region

Tatyana M. Petrova; Alexander M. Solodov; Alexander A. Solodov; Vladimir. M. Deichuli; Vitaly. I. Starikov

P1.43. The use of spectral moments to simulate rototranslational collision-induced bandshapes

Sergei Lokshtanov; Daniil Chistikov; Artem Finenko; Yulia Kalugina; Sergey Petrov; Andrey Vigasin

P1.44. The high resolution far infrared spectrum of ¹⁸O enriched water vapor at the SOLEIL synchrotron

Mikhail Tretyakov; Semen Mikhailenko; Tatiana Odintsova; Olivier Pirali; Pascale Roy; Alain Campargue

P1.45. Global deperturbation treatment of 5¹Σ⁺_u and 5¹Π_u states in Rb₂

Asen Pashov; Anna Grochola; Jacek Szczepkowski; Pawel Kowalczyk; Włodzimierz Jastrzebski

P1.46. Revealing the multiple structures of Glutamine

Iker León; Elena Rita Alonso; Carlos Cabezas; Santiago Mata; José Luis Alonso

P1.47. Linear Rayleigh and Raman scattering to second order

Robert Cameron; [Neel Mackinnon](#)

P1.48. The CRDS spectrum of natural and ^{13}C enriched carbon dioxide in the 1.73 μm window

[Ekaterina Karlovets](#); Anna Sidorenko; Peter Čermák; Didier Mondelain; Samir Kassi; Valery Perevalov; Alain Campargue

P1.49. Rotational spectroscopy of organophosphorus chemical agents: Cresyl and Phenyl Saligenin Phosphate

[Marcos Juanes San Jose](#); Rizalina T. Saragi; José L. Abad; Alberto Lesarri; Ruth Pinacho; José E. Rubio

P1.50. FTIR laboratory measurement of O I spectra in the 0.77–12.5 μm spectral range: Rydberg states and oscillator strengths

[Vladislav E. Chernov](#); Svatopluk Civiš; Petr Kubelík; Adam Pastorek; Ekaterina Zanozina; Vladislav Chernov; Alexander Naskidashvili

P1.51. Structural determination of aroma molecules in the gas-phase

[Rihab Hakiri](#)

P1.52. High resolution study of the strongly interacting $\nu_3(\text{F}_2)/\nu_1(\text{A}_1)$ bands of $^{28}\text{SiD}_4$

[Natalia I. Raspopova](#); Olga V. Gromova; Elena S. Bekhtereva; Sigurd Bauerecker; Christian Sydow; Oleg N. Ulenikov

P1.53. Molecular spectroscopy using radio-acoustic detection and high power radiation in THz region

Mikhail Tretyakov; German Golubiatnikov; [Maxim Koshelev](#); Alexander Tsvetkov; Andrey Fokin; Mikhail Glyavin

P1.54. Temperature dependence of collisional parameters of water 183-GHz line

Mikhail Tretyakov; [Maxim Koshelev](#); Ilya Vilkov

P1.55. Production of theoretical line lists for polyatomic molecules: SiH_4 , C_2H_4 , CH_3Cl , CH_3F , C_2H_2 , NH_3 , OH_3^+ , P_2H_2

[Sergei N. Yurchenko](#); Jonathan Tennyson; Barry P. Mant; Alec Owens; Phillip Coles; Andrey Yachmenev; Alexander Fateev; Vladlen Melnikov

P1.56. Indole rotational spectra

[Karel Vávra](#); Kateřina Luková; Jan Koucký; Patrik Kania; Štěpán Urban

P1.57. The visible spectrum of AlD^+ : the experimental and theoretical treatment

[Rafal Hakalla](#); Wojciech Szajna; Keith Moore; Ian Lane; Malgorzata Ostrowska-Kopec; Izabela Piotrowska; Przemyslaw Kolek; Mirosław Zachwieja; Ryszard Kepa

P1.58. High-resolution Fourier-transform spectroscopy of the comet-tail system in the $^{12}\text{C}^{17}\text{O}^+$ ion

[Rafal Hakalla](#); Izabela Piotrowska; Malgorzata Ostrowska-Kopec; Wojciech Szajna; Przemyslaw Kolek; Marcin Rusznica; Mirosław Zachwieja; Ryszard Kepa

P1.59. Self-broadening coefficients of rotational transitions of H_2S measured by submillimeter-wave spectroscopy

[Meriem Mouelhi](#); François Rohart; Francis Hindle; Cédric Bray; Gaël Mouret; Robin Bocquet; Hassen Aroui; Arnaud Cuisset

P1.60. Photodissociation dynamics of CF_3I in solution

[Manho Lim](#)

P1.61. Influence of the epigenetics marks in the non-covalent interactions between amino acids and DNA

[Rodrigo Martínez](#); José A. Fernández; Judith Millán

P1.62. Investigation on the degree of dissociation of Hydrogen plasma in PIG ion source via optical emission spectroscopy

[Seyed Shahab Odin Salimi](#); Masoud Mahjour Shafiei; Masoomeh Yarmohammadi Satri

P1.63. The optimal origin for computation of wave functions of polar molecules

[Anastasiia Chervinskaia](#); Dmitriy Dorofeev; Sergey Elfimov

Wednesday, September 5, 2018

Morning Sessions

	Plenary Session		
	Chair: Agnes Perrin , <i>Laboratoire de Meteorologie Dynamique</i>		
9:00–9:45	Plenary Lecture 5		
Mitxelena Auditorium	PT5. Spectroscopy for satellite remote sensing of greenhouse gases: recent advances and outstanding challenges		
	Vivienne Payne , <i>Jet Propulsion Laboratory – NASA</i>		
9:45–10:30	Plenary Lecture 6		
Mitxelena Auditorium	PT6. Odorants and broadband rotational spectroscopy: what can we learn?		
	Maria E. Sainz , <i>King's College London</i>		
10:30–11:00	Coffee Break		
Main Hall	Sponsors Stands will be placed at Main Hall		
	Oral Sessions 5		
11:00–12:40	Oral Session A5:	Oral Session B5:	Oral Session C5:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Vladimir Tyuterev , <i>University of Reims</i>	Chair: Mikhail Tretyakov , <i>Institute of Applied Physics –RAS</i>	Chair: Sang Kuk Lee , <i>Pusan National University</i>
	SPECTRAL SIMULATION AND DATABASES	LARGE MOLECULES: MW	NITROGEN AND WATER CLUSTERS
11:00–11:20	A5.1. Spectroscopic databases for the VAMDC and dat@osu portals	B5.1. High-resolution rotational spectroscopy of 3-Methylbutyronitrile – a molecule of astrophysical interest	C5.1. Microwave spectrum and nuclear quadrupole structure analysis of the NH ₃ –N ₂ van der Waals complex
	Vincent Boudon , <i>Univ. Bourgogne Franche-Comté</i>	Nadine Wehres , <i>University of Cologne</i>	Leonid Surin , <i>Institute of Spectroscopy RAS</i>
11:20–11:40	A5.2. Computing spectra of open-shell diatomic molecules with duo	B5.2. Solving discrepancies between theory and experiment: Methyl Jasmonate and Zingerone	C5.2. New millimeter-wave study of the CO–N ₂ van der Waals complex
	Sergey Yurchenko , <i>University College London</i>	Isabelle Kleiner , <i>LISA / CNRS</i>	Ivan Tarabukin , <i>Institute of Spectroscopy RAS</i>
11:40–12:00	A5.3. Accurate CO ₂ Raman spectral simulation: an algebraic alternative based on anharmonic ladder operators	B5.3. Polyalcohols as artificial sweeteners: signs of a sweetness–structure connection	C5.3. Microsolvation of ethyl carbamate conformers: a rotational spectroscopy study
	Miguel Carvajal , <i>Universidad de Huelva</i>	Elena R. Alonso , <i>Universidad de Valladolid</i>	Pablo Pinacho , <i>Universidad de Valladolid</i>
12:00–12:20	A5.4. Chiral rotational spectroscopy	B5.4. Microwave spectroscopic and quantum chemical investigations on 2-Acetylthiophene	C5.4. Study of the molecular structure and microsolvation (H ₂ O N=1–3) of 2-Phenylpyridine by rotational spectroscopy
	Jörg B. Götze , <i>University of Glasgow</i>	Christina Dindic , <i>IPC RWTH Aachen University</i>	Alberto Macario , <i>Universidad de Valladolid</i>

12:20–12:40	A5.5. Proton transfer tunneling splittings and the imaginary mode Hamiltonian: the beginning of a beautiful friendship	B5.5. Structure and rotational spectral features of N-Bu-tyraldehyde oxime: a study using MB-FTMW	C5.5. Structures of the complexes of Cyclooctanone with water
	Antonio Fernández-Ramos , <i>Universidade de Santiago de Compostela</i>	Nobuhiko Kuze , <i>Sophia University</i>	Ecaterina Burevschi , <i>King's College London</i>
13:00–14:30	Lunch Break		
	Iberdola tower (black tickets) or Deusto Library (white tickets)		

Afternoon Sessions

	Oral Session 6		
14:30–15:50	Oral Session A6:	Oral Session B6:	Oral Session C6:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Nobuhiko Kuze , <i>Sophia University</i>	Chair: Masaru Fukushima , <i>Hiroshima City University</i>	Chair: Bruno Martínez-Haya , <i>Universidad Pablo de Olavide</i>
	MOLECULAR STRUCTURE	CHIRPED–PULSED, LAMB–DIP AND IMAGING	CLUSTERS: IR
14:30–14:50	A6.1. Microwave spectrum and equilibrium structure of Diphenyl Disulfide	B6.1. Precise lamb-dip studies of monodeuterated Methanol	C6.1. Infrared spectrum and intermolecular potential energy surface of the CO–O ₂ dimer
	Jean Demaison , <i>University of Ulm</i>	Alexander Lapinov , <i>Institute of Applied Physics of the RAS</i>	Andrew R. McKellar , <i>National Research Council of Canada</i>
14:50–15:10	A6.2. Semi-experimental structure of vinyl acetate determined by microwave spectroscopy and ab initio methods	B6.2. State-to-state rotational rate coefficients for NH ₃ –NH ₃ collisions obtained with pump-probe chirped-pulse experiments	C6.2. Production and study of ionic clusters by photodissociation spectroscopy
	Stefanie Genuit , <i>Leibniz Universität Hannover</i>	Christian Endres , <i>MPI for Extraterrestrial Physics</i>	Raghdh Bejjani , <i>Université catholique de Louvain</i>
15:10–15:30	A6.3. Pure rotational spectrum of ¹⁵ ND and isotopic-independent Dunham-type analysis of imidogen radical	B6.3. Chirped-pulse millimetre-wave spectrometer for the 140–180 GHz region	C6.3. Unravelling non-covalent interactions in DNA-base ... Xanthine clusters
	Luca Bizzocchi , <i>Max-Planck-Institut für extraterrestrische Physik</i>	Clément Lauzin , <i>Université catholique de Louvain</i>	Ander Camiruaga , <i>Universidad del País Vasco (UPV/EHU)</i>
15:30–15:50	A6.4. Rotational spectroscopy of the two higher energy conformers of 2-cyanobutane	B6.4. Wave-packet imaging spectroscopy of the nitrogen dimer	C6.4. High-resolution spectroscopic study of the water-carbon dioxide van der Waals complex in the near-infrared range
	Marius Hermanns , <i>University of Cologne</i>	Yasuhiro Ohshima , <i>Tokyo Institute of Technology</i>	Clément Lauzin , <i>Université catholique de Louvain</i>
17:00–19:00	XXV Jubilee Session – Guggenheim Museum Joyful Pursuit of Molecular Dynamics and Spectra Dudley R. Herschbach , <i>Harvard University</i>		
19:00–20:00	Optional Guggenheim Museum Visit (reduced admittance fee)		

Thursday, September 6, 2018

Morning Sessions

	Plenary Session		
	Chair: Leonid Sinitsa , Zuev Institute of Atmospheric Optics – RAS		
9:00–9:45	Plenary Lecture 7		
Mitxelena Auditorium	PT7. Correlated rotational alignment spectroscopy: high-resolution, absolute frequency spectroscopy in the time domain		
	Thomas Schultz , <i>Ulsan National Institute Standards and Technology</i>		
9:45–10:30	Plenary Lecture 8		
Mitxelena Auditorium	PT8. Space exploration of Venus, Mars and beyond using (relatively) high resolution spectroscopy		
	Ann Carine Vandaele , <i>Royal Belgian Institute for Space Aeronomy</i>		
10:30–11:00	Coffee Break		
Main Hall	Sponsors Stands will be placed at Main Hall		
	Oral Sessions 7		
11:00–12:40	Oral Session A7:	Oral Session B7:	Oral Session C7:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Vincent Boudon , <i>ICB Bourgogne – CNRS</i>	Chair: Qian Gou , <i>Chongqing University</i>	Chair: Tom Varberg , <i>Macalester College</i>
	SPECTRAL MODELLING	HOMOCLUSTERS	CALIBRATION, DATABASES AND SOFTWARE
11:00–11:20	A7.1. Universal behaviour of diatomic halo states and mass sensitivities of their properties	B7.1. Observation of two dimers of phenyl ethyl alcohol using rotational spectroscopy	C7.1. Application of molecular spectroscopic databases for certification of calibration gas mixtures
	Vladimir Spirko , <i>Academy of Sciences of the Czech Republic</i>	Rizalina T. Saragi , <i>Universidad de Valladolid</i>	Vitaly Beloborodov , <i>D.I. Mendeleev Institute for Metrology</i>
11:20–11:40	A7.2. High energy states of polyatomic molecules: application to hot spectra	B7.2. Self-aggregation process in CH ₂ F ₂ : large homo-clusters studied by rotational spectroscopy	C7.2. Comb-calibrated coherent Raman spectroscopy of molecular hydrogen
	Vladimir Tyuterev , <i>University of Reims</i>	Camilla Calabrese , <i>Universidad del País Vasco (UPV/EHU)</i>	Davide Gatti , <i>IFN/CNR & Politecnico di Milano</i>
11:40–12:00	A7.3. Absolute vibrational assignment from fragmentary spectroscopic data in two isotopologues	B7.3. The nitrogen–nitrogen noncovalent interaction in the gas phase	C7.3. Design and fabrication of a high-resolution Fourier-transform spectrometer with a supercontinuum laser source
	Asen Pashov , <i>Sofia University St. Kliment Ohridski</i>	Lorenzo Spada , <i>Scuola Normale Superiore</i>	Clément Lauzin , <i>Université catholique de Louvain</i>

12:00–12:20	A7.4. Atmospheric oxygen mm-absorption: models review and uncertainties evaluation	B7.4. Understanding structural similarities in the Homodimers of Fluorene, Dibenzofuran and Diphenylether via broadband rotational spectroscopy	C7.4. Line intensities for the ν_6 and $2\nu_3$ bands of Methyl Iodide ($^{12}\text{CH}_3\text{I}$)
	Dmitriy Makarov , <i>Institute of Applies Physics</i>	Mariyam Fatima , <i>Deutsches Elektronen-Synchrotron</i>	Agnes Perrin , <i>Laboratoire de Meteorologie Dynamique</i>
12:20–12:40	A7.5. Anharmonic IR spectra of chemical warfare agents from ab initio molecular dynamics simulations	B7.5. Investigation of the products of thermal self-polymerization of Methyl methacrylate by means of microwave spectroscopy – the rotational spectrum of the dimer	C7.5. Automatic assignment and fitting of spectra with PGOPHER
	Pawel Rodziewicz , <i>University of Bialystok</i>	Sven Herbers , <i>Leibniz Universität Hannover</i>	Colin Western , <i>University of Bristol</i>
13:00–14:30	Lunch Break		
	Iberdola tower (black tickets) or Deusto Library (white tickets)		

Afternoon Sessions

	Oral Session 8		
14:30–15:50	Oral Session A8:	Oral Session B8:	Oral Session C8:
	Mitxelena Auditorium	Baroja Auditorium	Oteiza Auditorium
	Chair: Pierre Carçabal , <i>Institut des Sciences Moléculaires d'Orsay CNRS</i>	Chair: Dennis W. Tokaryk , <i>University New Brunswick</i>	Chair: José Luis Doménech , <i>Instituto de Estructura de la Materia CSIC</i>
	MATRIX AND CONDENSED PHASES	CAVITY RING-DOWN	CLUSTERS: IR
14:30–14:50	A8.1. Does one need a high resolution in matrix isolation studies? the symmetry changes of the $^{28}\text{SiH}_4$ molecule in low-temperature matrixes	B8.1. Wavelength-meter controlled cavity ring-down spectroscopy for measurement of trace water vapor at ppt levels	C8.1. High resolution infrared laser jet-cooled spectroscopy of small van der Waals clusters with rare gases
	Ruslan Asfin , <i>Saint Petersburg State University</i>	Hisashi Abe , <i>National Metrology Institute of Japan (NMIJ)</i>	Pierre Asselin , <i>CNRS</i>
14:50–15:10	A8.2. Gas to solid phase transition of theobromine: crystal vs amorphous structures	B8.2. CRDS of the collision induced absorption (CIA) band of O_2 at 1.27 μm	C8.2. Insights into the binding of protons, cations and anions by azamacrocycles
	Imanol Usabiaga , <i>Università di Bologna</i>	Alain Campargue , <i>CNRS/ Université de Grenoble</i>	Bruno Martinez-Haya , <i>Universidad Pablo de Olavide</i>
15:10–15:30	A8.3. Seeing more does not necessarily mean seeing clearly	B8.3. Cavity-enhanced dispersion spectroscopy for the highest accuracy applications	C8.3. Infrared spectroscopy and quantum-chemical calculations on diacetylene complexes: a joint experimental study and theoretical investigation on $\text{OCS-H}_2\text{C}_4$ and $\text{N}_2\text{O-H}_2\text{C}_4$ dimers
	Ilya Shenderovich , <i>University of Regensburg</i>	Daniel Lisak , <i>Nicolaus Copernicus University</i>	Andrea Pietropolli , <i>Università Ca' Foscari Venezia – Dipartimento Scienze Molecolari e Nanosistemi</i>

15:30–15:50	A8.4. Titania- and montmorillonite- photocatalyzed synthesis of methane from carbon dioxide and the subsequent formation of nucleobases on early Mars and Earth	B8.4. H ₂ -He scattering states observation with cavity ring-down spectroscopy	C8.4. Infrared spectra of the carbon monoxide – water dimer and larger clusters
	Svatopluk Civiš , <i>J. Heyrovsky Institute of Physical Chemistry</i>	Magdalena Konefať , <i>Nicolaus Copernicus University in Toruń</i>	N. Moazzen-Ahmadi , <i>University of Calgary</i>
16:00–18:30 Axular Room and Chillida Room	Poster Session 2 (P2.1. a P2.63.) and Coffee Break		
19:00 –20:00 Meeting point: Maritime Museum, 7 pm	Boat Tour		

Poster presentations – Session 2

P2.1. The Rotational study of vitamin B6 form pyridoxine

Elena Rita Alonso; Iker León; Lucie Kolesníková; Santiago Mata; José L. Alonso

P2.2. Rotational spectrum of Methoxy Acetaldehyde: a combined CP-FTMW and millimeter wave study

Lucie Kolesníková; Isabel Peña; Elena R. Alonso; Belén Tercero; José Cernicharo; Santiago Mata; José L. Alonso

P2.3. Conformational study of Cyclooctanone using broadband rotational spectroscopy

Ecaterina Burevschi; Isabel Peña; Maria Eugenia Sanz

P2.4. The monohydrate and dimer of Phenyl Ethyl Mercaptan by rotational spectroscopy

Rizalina Tama Saragi; Marcos Juanes; Alberto Lesarri; Ruth Pinacho; José E. Rubio

P2.5. Spectroscopy group at the University of the Basque Country

Camilla Calabrese, Aran Insausti; Maider Parra, Cristobal Pérez, Iciar Uriarte, Imanol Usabiaga, Emilio J. Cocinero; Francisco J. Basterretxea

P2.6. Nuclear spin conversion of ammonia isolated in noble gas matrices

Haruka Nagamoto; Takeru Sugimoto; Ichiro Arakawa; Koichiro Yamakawa

P2.7. Simulation of rotational energy levels of the ground and first excited vibrational states of H₂S and SO₂ molecules using the effective Hamiltonian approach

Irina Vasilenko; Olga Naumenko; Alexander Bykov

P2.8. Analytical extension of hard-collision model of velocity-changing collisions in the Hartmann-Tran profile

Magdalena Konefať; Michał Słowiński; Mikołaj Zaborowski; Daniel Lisak; Piotr Wcisło

P2.9. Far- and mid-infrared spectroscopy of matrix-isolated clusters and matrix-sublimated ice of D₂O

Hirokazu Nasu; Kazuki Niwata; Yuichi Azuma; Toshiya Tanaka; Ichiro Arakawa; Koichiro Yamakawa

P2.10. Laser absorption spectroscopy of ¹³CH₄ at 80 K and 296 K near 1.73 μm

Magdalena Konefať; Mélanie Ghysels; Didier Modelain; Samir Kassi; Alain Campargue

P2.11. Nuclear spin conversion in matrix-isolated water monomer and dimer

Koichiro Yamakawa; Kiwa Yamaguchi; Ichiro Arakawa

P2.12. Understanding metal compound chemistry in Late-Type star environments using chirped-pulse FT millimeter Wave Spectroscopy of supersonic Jets

[Pascal Stahl](#); Guido W. Fuchs; Thomas F. Giesen

P2.13. Tropospheric reactions of triazoles with hydroxyl radicals

[Najoua Derbel](#); Olfa Ferchichi; Alexander Alijah

P2.14. Flexibility at the fringes: conformations of the steroid hormone β -estradiol

[Sabrina Zinn](#); Melanie Schnell

P2.15. Franck-Condon simulated electronic spectra of gold carbene complexes

[Agnes H H Chang](#); Bing Jian Sun; Ian J. Lin

P2.16. FTIR measurements of the third overtone band of $^{12}\text{C}^{16}\text{O}$

[Gang Li](#); Alexandra Domanskaya; Alekandra Kyuberis; Volker Ebert

P2.17. High resolution Ro-Vibrational analysis of C_2HD_3 in the region of $600 - 1150 \text{ cm}^{-1}$

Olga Gromova; Nadezda V. Kashirina; [Elena S. Bekhtereva](#); Sigurd Bauerecker; Christian Sydow; Oleg N. Ulenikov

P2.18. Fourier transform spectrum of $^{34}\text{SO}_2$ in the region of the ν_2 bending fundamental band

[Anastasiia G. Ziatkova](#); Olga V. Gromova; Elena S. Bekhtereva; Sigurd Bauerecker; Christian Sydow; Georg Mellau; Martin Quack; Oleg N. Ulenikov

P2.19. Realistic vibrational spectra of Ethylene Based on a 3-band model

[Sergey Yurchenko](#); Barry Mant; Jonathan Tennyson; Andrey Yachmenev

P2.20. Line positions and strengths in the ν_{10}/ν_7 bands of the C_2D_4 molecule

[Anna Fomchenko](#); Elena S. Bekhtereva; Olga V. Gromova; Maria A. Merkulova; Sigurd Bauerecker; Christian Sydow; Oleg N. Ulenikov

P2.21. Direct deperturbation analysis of the L-mixed $\text{B}^1\Pi$ and $\text{C}^1\Sigma^+$ states of LiRb

[Ekaterina Bormotova](#); Elena Pazyuk; Andrei Stolyarov; Asen Pashov

P2.22. High resolution study of the decades of H_2S

Tolganay Yersin; Fangece Zhang; [Elena S. Bekhtereva](#); Olga V. Gromova; Sigurd Bauerecker; Christian Sydow; Oleg N. Ulenikov

P2.23. Absolute line strengths in bands ν_9 and ν_{11} of the $^{12}\text{C}_2\text{H}_4$ molecule

[Yulia S. Aslapovskaya](#); Aleksei V. Kuznetsov; Olga V. Gromova; Elena S. Bekhtereva; Sigurd Bauerecker; Christian Sydow; Oleg N. Ulenikov

P2.24. Analysis of resonance interactions in the bands located in the region of $1500 - 1750 \text{ cm}^{-1}$ in the $\text{C}_2\text{H}_2\text{D}_2$ -cis molecule

Yuliya V. Konova; Ivan A. Konov; [Olga V. Gromova](#); Elena S. Bekhtereva; Sigurd Bauerecker; Christian Sydow; Oleg N. Ulenikov

P2.25. High resolution study of $^{73}\text{GeH}_4$ in the dyad and pentade regions

[Natalia I. Raspopova](#); Olga V. Gromova; Elena S. Bekhtereva; Petr G. Sennikov; Maxim A. Koshelev; Irina A. Velmuzhova; Aleksandr P. Velmuzhov; Oleg N. Ulenikov

P2.26. High resolution study of Hexades of H_2MS

Fangece Zhang; Petr A. Glushkov; Anastasiia S. Belova; [Elena S. Bekhtereva](#); Olga V. Gromova; Sigurd Bauerecker; Christian Sydow; Christof Maul; Oleg N. Ulenikov

P2.27. First high resolution analysis of SiD_4 in the dyad region

Natalia Raspopova; [Olga V. Gromova](#); Elena S. Bekhtereva; Christian Sydow; Sigurd Bauerecker; Oleg N. Ulenikov

P2.28. Ab initio calculations of the potential energy curves and intramolecular interactions in LiRb and LiCs including spin-dependent effects

[Ekaterina Bormotova](#); Alexander Medvedev

P2.29. Comprehensive update of structural data in the MOGADOC database

Rainer Rudert; Natalja Vogt; [Jürgen Vogt](#)

P2.30. A highly accurate ab initio dipole moment surface for water: transitions extending into the ultraviolet

[Aleksandra Kiuberis](#); Eamon Conway; Oleg Polyansky; Irina Mizus; Jonathan Tennyson; Nikolay Zobov

P2.31. Far IR continuum absorption of H_2^{16}O and H_2^{18}O

Mikhail Tret'yakov; [Tatyana Odintsova](#); Aleksandra Zibarova; Olivier Pirali; Pascale Roy; Alain Campargue

P2.32. A complete and coherent spectral line parameter set for the full $2\nu_3$ -band of $^{14}\text{N}_2^{16}\text{O}$ including line strengths, air- and self-induced broadening and shift coefficients

[Gang Li](#); Viktor Werwein; Olav Werhahn; Volker Ebert

P2.33. Rovibrational laser jet-cooled spectroscopy of the $\text{NH}_3\text{--Ar}$ complex in the ν_2 umbrella region of NH_3 : comparison between new infrared data and an ab initio calculated spectrum

[Yacine Belkhdja](#); Pierre Asselin; Atef Jabri; Alexey Potapov; Jérôme Loreau; Ad van der Avoird

P2.34. Exploring interstellar chemical processes of polycyclic aromatic hydrocarbons using opposite sides of the electromagnetic spectrum

[Pragya Chopra](#); Donatella Loru; Sébastien Gruet; Amanda Steber; Hansjochen Köckert; Jasper Pechel; Jan Lahl; Sylvain Maclot; Jason Lee; Rebecca Boll; Simon Dörner; Sadia Bari; Benjamin Erk; Lanhai He; Mehdi Mohammad Kazemi; Alexander Lemmens; Felix Allum; Robert Mason; David Heathcote; Michael Burt; Dimitrios Rompotis; Pavel Olshin; Christopher Passow; Daniel Ramm; Farzaneh Ziaee; Xuemei Cheng; Nora Schirmel; Joss Wiese; Melby Johnny; Daniel Rolles; Sebastian Trippel; Terrence Mullins; Anouk Rijs; Jochen Küpper; Mark Brouard; Claire Vallance; Per Johnsson; Bastian Manschwe-tus; Melanie Schnell

P2.35. Laser-based hydrogen chloride measurements for biogas and biomethane applications

Javis Nwaboh; [Alexandra Domanskaya](#); Zhechao Qu; Olav Werhahn; Volker Ebert

P2.36. Bimolecular absorption in dry atmospheric gases at millimeter waves: new experimental data and high accuracy modeling

Mikhail Tret'yakov; [Evgeny Serov](#); Aleksandr Balashov; Tatyana Odintsova; Maksim Koshelev; Aleksandra Zibarova

P2.37. Exoplanetary atlas of molecular opacities: ExoMol Gallery

[Sergei N Yurchenko](#); Jonathan Tennyson; Oleg N. Polyansky; ExoMol team

P2.38. Advanced fitting method for mid-infrared spectra

[Risto Sarjonen](#); Teemu Kääriäinen; Albert Manninen

P2.39. Nuclear spin conversion among three isomers in crystal II methane measured by infrared spectroscopy

[Takeru Sugimoto](#); Hirokazu Nasu; Ichiro Arakawa; Koichiro Yamakawa

P2.40. LED-based Fourier transform spectroscopy of HD^{16}O and H_2^{16}O in 14800–15500 cm^{-1} spectral region

[Irina Vasilenko](#); Victor Serdyukov; Olga Naumenko; Leonid Sinitsa

P2.41. Collisional broadenings and shifts in the $S_0(0)$, $S_0(1)$ and $S_0(2)$ rotational lines of HD perturbed by He.

[Raúl Martínez Torres](#); Dionisio Bermejo; Franck Thibault; Piotr Wcisło

P2.42. Terahertz spectra of Ambroxol

[Jan Koucký](#); Tereza Uhlíková; Jitka Bartnická; Ivana Wurmová; Patrik Kania; Štěpán Urban

P2.43. Rotational spectra of 1,2,3,4-Tetrahydroquinoline

[Karel Vávra](#); Kateřina Luková; Patrik Kania; Štěpán Urban

P2.44. Evaluation of the current spectroscopic databases, such as GEISA-2015 and HITRAN-2016, in the frame of the preparation of the new release of GEISA

[Agnes Perrin](#); Raymond Armante; Nicole Jacquinet; Noelle Scott; Alain Chedin

P2.45. High-resolution FTIR spectrum of SO_2 molecule between 2400 and 2650 cm^{-1}

[Irina Vasilenko](#); Olga Naumenko; Veli-Matti Horneman

P2.46. Precision spectroscopy and global deperturbation analysis of the $\text{A}^1\Pi(v=0)$ state in $^{13}\text{C}^{18}\text{O}$

[Rafal Hakalla](#); Talluri Trivikram; Alan Heays; Edcel Salumbides; Nelson de Oliveira; Robert Field; Wim Ubachs

P2.47. Precision FT spectroscopy and deperturbation analysis of the $A^1\Pi(v=0)$ state in $^{12}\text{C}^{17}\text{O}$

Rafal Hakalla; Wojciech Szajna; Alan Heays; Nelson de Oliveira; Edcel Salumbides; Malgorzata Ostrowska-Kopec; Izabela Piotrowska; Przemyslaw Kolek; Mirosław Zachwieja; Ryszard Kepa; Robert Field; Wim Ubachs

P2.48. Cavity ring-down spectroscopy of CH in the UV

Chris Medcraft; Harold Linnartz; Wim Ubachs

P2.49. THz Spectroscopy: a solution to monitor spoilage indicators. The case of Atlantic salmon

Meriem Mouelhi; Lotta Kuuliala; Cédric Bray; Robin Bocquet; Arnaud Cuisset; Gaël Mouret; Frank Devlieghere; Francis Hindle

P2.50. Structure and dynamics of substituted imidazoles in the gas phase

Eva Gougoula; Nicholas R. Walker

P2.51. New spectral characterization of dimethylether isotopologues in the THz region

José M. Fernández; Guzmán Tejeda; Miguel Carvajal; M. Luisa Senent

P2.52. Ab Initio potential energy surface and vibration-rotation energy levels of Germanium Dicar-bide, GeC_2

Jacek Koput

P2.53. The influence of water vapor isotopologues on the reflection coefficient of multilayer mirrors

Leonid Sinitisa; Victor Serdyukov; Alexei Lugovskoi; Michail Arshinov

P2.54. H_2^{16}O and H_2^{18}O absorption spectra between 16,460 and 17,200 cm^{-1}

Leonid Sinitisa; Semen Mikhailenko; Victor Serdyukov

P2.55. Monosulfur derivatives of methyl formate: millimeter and submillimeter wave spectra of S- and O-methyl thioformates

Vadym Ilyushyn; Atef Jabri; Roman Motiyenko; Laurent Margulès; Jean-Claude Guillemin; Olga Dorovskaya; Eugene Alekseev; Isabelle Kleiner; Belén Tercero; José Cernicharo

P2.56. Analyses of various ^{17}O and ^{18}O enriched isotopic species of ozone from FTS high resolution spectra

Vladimir Tyuterev; Evgeniya Starikova; Alain Barbe; Marie-Renée De Backer

P2.57. New version of S&MPO database on the ozone spectroscopy

Vladimir Tyuterev; Yurii Babikov; Semen Mikhailenko; Alain Barbe; Evgeniya Starikova

P2.58. Quantitative influence of the ozone potential energy surface upon dynamics of the $^{18}\text{O} + ^{32}\text{O}_2$ reaction

Vladimir Tyuterev; Grégoire Guillon; Pascal Honvault; Roman Kochanov

P2.59. Analysis and theoretical modelling of the ^{18}O enriched carbon dioxide spectrum by CRDS near 1.74 μm

Ekaterina Karlovets; Peter Čermák; Didier Mondelain; Samir Kassi; Alain Campargue; Sergey Tashkun; Valery Perevalov

P2.60. Electronic structure of the molecular system $\text{HPS}^+/\text{HSP}^+$

B. Mehnen, M. Hochlaf, Saida Ben Yaghlane

P2.61. A global approach for deperturbation of NiH lowest-lying electronic states

Ilvie Havalyova; Ivayla Bozhinova; Amanda Ross; Patrick Crozet; Asen Pashov

P2.62. Dispersed fluorescence from NiD excited with a CW laser, taken in a novel way with a BOMEM DA3 interferometer

Amanda J. Ross, Patrick Crozet, Bradley G. Guislain, Ryan A. R. Harvey, Allan G. Adam, Dennis W. To-karyk

P2.63. Observation of a periodic many-body system

Klaus Müller-Dethlefs, Francois Michels

P2.64. Creating, imaging, and controlling chiral molecules with electric fields

Andrey Yachmenev, Alec Owens, Jochen Küpper

Friday, September 7, 2018

Morning Sessions

	Plenary Session		
	Chair: Amanda Ross , <i>Université Lyon 1 & CNRS</i>		
9:00–9:45	Plenary Lecture 9		
Mitxelena Auditorium	PT9. Nature and strength of unconventional hydrogen bonds		
	Sanjay Wategaonkar , <i>Tata Institute of Fundamental Research</i>		
9:45–10:30	Plenary Lecture 10		
Mitxelena Auditorium	PT10. High resolution spectra of floppy molecules: neutral and ionic species		
	Koichi M. T. Yamada , <i>National Institute of Advanced Industrial Science and Technology</i>		
10:30–11:00	Coffee Break		
Main Hall	Sponsors Stands will be placed at Main Hall		
	Oral Sessions 9		
11:00–12:40	Oral Session A9:	Oral Session B9:	Oral Session C9:
	Mitxelena Auditorium	Baroja Auditorium	Otelza Auditorium
	Chair: Walther Caminati , <i>University of Bologna</i>	Chair: Thomas Giesen , <i>University of Kassel</i>	Chair: Francisco Basterretxea , <i>Universidad del País Vasco (UPV/EHU)</i>
	HALOGEN AND CHALCOGEN INTERACTIONS	ASTROPHYSICAL MOLECULES	BIOMOLECULES
11:00–11:20	A9.1. Effect of fluorine substitution on non-covalent interactions in molecular complexes of aromatic compounds	B9.1. Spectroscopy of new Imine astrophysics target: Methylimino-acetonitrile ($\text{CH}_3\text{N}=\text{CHCN}$)	C9.1. Rotational spectroscopy signature of smelling allyl alcohols
	Sonia Melandri , <i>University of Bologna</i>	Laurent Margules , <i>Laboratoire PhLAM UMR CNRS 8523</i>	Assimo Maris , <i>University of Bologna</i>
11:20–11:40	A9.2. Chalcogen bond formation: The non-covalent, intermolecular sulfur-sulfur interaction of dimethyl sulfide and sulfur dioxide	B9.2. Imidazole rotation spectrum investigation for astrophysical search	C9.2. DNA sugars: in the gas phase and in solution
	Daniel Obenchain , <i>Leibniz Universität Hannover</i>	Barbara Michela Giuliano , <i>Max-Planck-Institut für extraterrestrische Physik</i>	Iciar Uriarte , <i>Universidad del País Vasco (UPV/EHU)</i>
11:40–12:00	A9.3. Halogen bond and internal dynamics in Perfluorocyclobutane-water	B9.3. Laboratory rotational spectroscopy of isotopic species of Methyl Mercaptan, $\text{CH}_3^{34}\text{SH}$ and CH_3SD , and search for them in ISM	C9.3. Multiresponsive chromic soft materials: formation of macrocycles from carbazole-based biradicaloids
	Qian Gou , <i>Chongqing University</i>	Olena Zakharenko , <i>I. Physikalisches Institut, Universität zu Köln</i>	Maria Carmen Ruiz , <i>Universidad de Málaga</i>

12:00–12:20	A9.4. Rotational spectroscopy of the dimers and mono-hydrates of furfuryl alcohol and thenyl alcohol	B9.4. Accurate millimetre and submillimetre rest frequencies for cis- and trans-dithioformic acid, HCSSH	C9.4. Raman spectroscopy as a versatile tool to study organic biradicals
	Marcos Juanes, <i>Universidad de Valladolid</i>	Domenico Prudeniano, <i>Max-Planck-Institut für extraterrestrische Physik</i>	Jose Luis Zafra, <i>Universidad de Málaga</i>
12:20–12:40	A9.5. Microwave spectroscopic characterization of the S...O/N chalcogen bond	B9.5. The nanocosmos gas cell: A broadband Fourier transform millimeterwave spectrometer based on radio astronomy receivers.	C9.5. Molecular spectroscopic study on a natural uric acid type of Kidney Stone
	Gang Feng, <i>Chongqing University</i>	Celina Bermúdez, <i>Instituto de Física Fundamental CSIC</i>	Mustafa Kumru, <i>University of Freiburg</i>
13:00–14:30	Lunch Break		
	Iberdola tower (black tickets) or Deusto Library (white tickets)		
14:30–15:30	Science Salon: Discussion Forum for students		
Mitxelena Auditorium	Informal meeting with Dudley R. Herschbach, Nobel Laureate in Chemistry, 1986		

Free Afternoon

21:00–24:00	Conference Dinner
	Euskalduna Concert Hall
	<p>Including:</p> <ul style="list-style-type: none"> – Award of the Pliva Prize, Prizes of the University of Valladolid and PCCP Prize to the best oral presentations from students – Award of the International Mez–Starck Prize 2018 of the Dr. Barbara Mez–Starck Foundation for the Advancement of Science and Research. – Announcement of the 20 student travel grant recipients.

Conference abstracts

Plenary talks

In the following pages all conference abstracts have been ordered by day and session.

The abstract numbers correspond to the daily scientific program in page 12.

You can search for specific authors in the author index at the end of this abstract book (all authors and co-authors are listed in alphabetical order with their abstract number/s).

Collision-induced spectra of oxygen and nitrogen molecules

Tijs Karman², Gerrit C. Groenenboom¹, Ad van der Avoird¹

1) Theoretical Chemistry, Institute for Molecules and Materials,
Radboud University, Nijmegen, The Netherlands

2) Department of Chemistry, Durham University,
South Road, Durham DH1 3LE, United Kingdom

Collision-induced absorption is the phenomenon that interactions between colliding molecules lead to absorption of light, even for transitions that are forbidden for the isolated molecules. Collision-induced absorption contributes to the atmospheric heat balance and is important for the electronic excitations of O₂ that are used for remote sensing. Absorption by O₂-O₂ pairs has been put forward as a biomarker to be observed in exoplanetary transit spectra.

First, we studied the roto-translational spectrum of N₂-N₂ collision complexes using quantum mechanical line-shape calculations [1, 2]. Apart from some work on effectively isotropic systems such as H₂-H₂ and H₂-He, such calculations have always been performed with the approximation that the interaction potential between the colliding molecules is isotropic. We developed a scattering approach by which we could fully include the interaction anisotropy and we demonstrated that this anisotropy increases the line strength and brings our calculations in closer agreement with experimental spectra.

Next, we performed an ab initio study of the $X^3\Sigma_g^- \rightarrow a^1\Delta_g$ and $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ electronic transitions of O₂, which are electric-dipole forbidden by both spin and spatial selection rules [3–5]. We unambiguously identified the underlying absorption mechanism, which –contrary to textbook knowledge– is shown to depend explicitly on the collision partner: N₂ or O₂. This explains experimentally observed qualitative differences between O₂-O₂ and O₂-N₂ collision-induced spectra in the overall intensity, line shape, and vibrational dependence of the absorption spectrum. Moreover, we provided explicit analytical expressions for the spectral line shape depending on the underlying mechanism, which can be applied in the calibration of satellite spectrometers that probe various gases in the atmosphere.

[1] T. Karman, A. van der Avoird, and G. C. Groenenboom, J. Chem. Phys. 142, 084305 (2015).

[2] T. Karman, E. Millardos, K. L. C. Hunt, G. C. Groenenboom, and A. van der Avoird, J. Chem. Phys. 142, 084306 (2015).

[3] T. Karman, A. van der Avoird, and G. C. Groenenboom, J. Chem. Phys. 147, 084306 (2017).

[4] T. Karman, A. van der Avoird, and G. C. Groenenboom, J. Chem. Phys. 147, 084307 (2017).

[5] T. Karman, M. A. J. Koenis, A. Banerjee, D. H. Parker, I. E. Gordon, A. van der Avoird, W. J. van der Zande, and G. C. Groenenboom, Nature Chem. 10, 549 (2018).

Spectroscopy of Molecular Radicals in Helium Droplets

PT2:

Gary Douberly

University of Georgia, Athens, Georgia, United States

Catalytic thermal cracking of O_2 is employed to dope helium droplets with $O(^3P)$ atoms.^[1] Mass spectrometry of the doped droplet beam reveals an O_2 dissociation efficiency larger than 60%; approximately 26% of the droplet ensemble is doped with single oxygen atoms. Sequential capture of $O(^3P)$ and HCN leads to the production of a hydrogen-bound O–HCN complex in a 3S electronic state, as determined *via* comparisons of experimental and theoretical rovibrational Stark spectroscopy. *Ab initio* computations of the three lowest lying intermolecular potential energy surfaces reveal two isomers, the hydrogen-bound (3S) O–HCN complex and a nitrogen-bound (3P) HCN–O complex, lying 323 cm^{-1} higher in energy. The non-relativistic HCN–O to O–HCN interconversion barrier is predicted to be only 42 cm^{-1} . Moreover, the barrier is reduced upon explicit consideration of spin–orbit coupling. Consistent with the prediction of a relatively small interconversion barrier, there is no experimental evidence for the production of the nitrogen-bound species upon sequential capture of $O(^3P)$ and HCN.

[1] Brice, J. T.; Franke, P. R.; Douberly, G. E. *J. Phys. Chem. A*, **2017**, 121, 9466.

Beryllium bonding probed by anion photodetachment spectroscopy

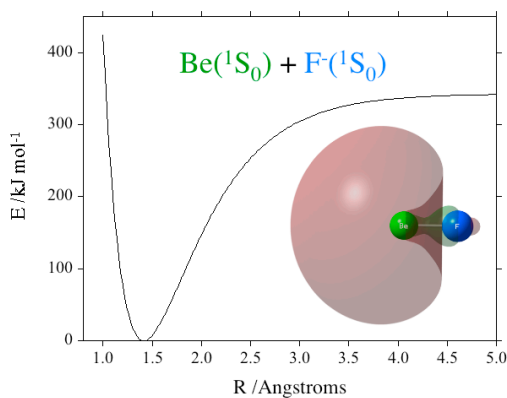
M. L. Green, A. B. Dermer, K. J. Mascaritolo and M. C. Heaven

Department of Chemistry, Emory University, Atlanta, GA 30322

PT3.

The chemistry of beryllium is known to be significantly different from the behavior exhibited by the heavier group IIA elements. Due to its high ionization energy and small size, the bonding of beryllium is significantly more covalent than the bonds of typical group IIA metals. As a consequence, beryllium and its compounds exhibit unique properties. However, the chemistry of beryllium is underexplored due to its toxicity. To circumvent this problem there have been many theoretical studies of beryllium and its compounds. Being a light element with just four electrons, beryllium appears to be well suited for investigation using non-relativistic quantum chemical methods. However, calculations for Be-compounds frequently prove to be difficult due to subtle (but dominant) electron correlation effects.

We are currently studying a series of BeX diatomics by means of anion autodetachment spectroscopy to examine the bonding. BeX⁻ anions are generated by pulsed laser ablation, mass selected and then photodetached. Electron imaging and autodetachment techniques are used to recover spectroscopic data. Recent results for the BeO⁻, BeS⁻ and BeF⁻ anions will be presented. BeO⁻ and BeS⁻ both exhibit dipole-bound excited states, permitting the observation of rotationally resolved spectra. BeF⁻ shows an unusually strong bond between the closed-shell Be and F⁻ moieties. Electronic structure calculations, validated by comparison with the spectroscopic observations, have been used to examine the bonding in the anionic and neutral species.



Which spectroscopy to study astro-PAHs?

PT4.

Christine Joblin

IRAP, CNRS/University Toulouse

Polycyclic aromatic hydrocarbons (PAHs) absorb UV radiation from stars and play a key role in the physical and chemical evolution of astronomical objects. Following the absorption of UV photons, radiative cooling gives rise to the aromatic infrared bands (AIBs) that are observed in emission in many regions of space. Although PAHs should contain at least 10% of the carbon in the Galaxy, no individual molecule of this family could be identified so far.

Interstellar PAHs are expected to contribute to the 220 nm bump and the far-UV rise of the extinction curve [1]. They could be the carriers of (some of) the diffuse interstellar bands (DIBs) [2]. In addition of the AIBs that fall in the mid-IR, bands are expected in the far-IR range [3]. Rotational lines should also be present in the mm-cm range, especially for molecules, which carry a significant dipole moment [4]. Various laboratory setups and spectroscopic techniques are required to ultimately mimic a collision free environment and sample a range of temperatures from hot (~1000 K) for the AIBs, to warm/ cold for rotational lines, to cold (~10 K) for the DIBs.

In this talk, I will summarise the status of this field in the various spectral ranges, emphasising the synergy between laboratory astrophysics activities (e.g [5, 6]) and recent/coming observational investigations. These make use of ground-based telescopes [7] and radiotelescopes [8, 9], as well as of space missions such as *Herschel* [10], and the coming James Webb Space Telescope [11]. I will then discuss the importance of guiding these spectroscopic studies by experiments in which the formation and evolution of large carbonaceous molecules under astrophysical conditions are simulated, notably as part of the ERC Synergy project Nanocosmos [12].

-
- [1] Joblin C., Léger A., and Martin P., *Astrophys. J.*, 1992, 393, L79
 - [2] Salama F., Galazutdinov G. A., Krelowski J., et al. *Astrophys. J.*, 2011, 728, 154
 - [3] Mulas G., Mallocci G., Joblin C., Toubanc D., *Astron.&Astrophys.*, 2006, 460, 93
 - [4] Rouan D., Léger A., Omont A., Giard M., *Astron.&Astrophys.*, 1992, 253, 498
 - [5] Campbell E.K., Holz M., Gerlich D., and Maier J.P., 2015, *Nature* 523, 322
 - [6] Chakraborty S., Mulas G., Demyk K., Joblin C., submitted
 - [7] Cox, N.L.J., Cami, J., Farhang A., et al., *Astron.&Astrophys.*, 2017, 606, id.A76
 - [8] Pilleri P., Herberth D., Giesen T.F., et al., *Mon.Not.Roy.Astron.Soc.*, 2009, 397, 1053
 - [9] McGuire B.A., Burkhardt A.M., Kalenskii S., et al., *Science*, 2018, 359, 202
 - [10] Joblin C., Mulas G., Mallocci G., et al., *EAS Pub. Series*, 2011, 46, 123
 - [11] www.jwst-ism.org
 - [12] <https://nanocosmos.iff.csic.es/>

Spectroscopy for satellite remote sensing of greenhouse gases: Recent advances and outstanding challenges

Vivienne H. Payne¹, Brian J. Drouin¹, Fabiano Oyafuso¹, David Crisp¹, Alexandre Guillaume¹, Brendan Fisher¹, Joseph T. Hodges², Erin Adkins², David A. Long², Elizabeth Lunny³, Gautam Stroschio³, Mitchio Okumura³, Eli J. Mlawer⁴

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Satellite observations can complement measurements from ground-based networks and airborne campaigns to provide new insights into the spatial and temporal distribution of trace gases that are key to our understanding of atmospheric chemistry and Earth's climate. However, obtaining the trace gas information from satellite radiance measurements requires processing of the radiances using retrieval algorithms. The accuracy of remotely sensed quantities from such algorithms depends directly on the accuracy of the forward model used in the algorithm.

Retrievals of well-mixed greenhouse gases place particularly stringent demands on the accuracy of the forward model, since the variations of these gases in the atmosphere are small compared to the background. Systematic errors in the forward model can lead to regional-scale and/or time-dependent biases in the retrieval products, which in turn can lead to biases in estimates of sources and sinks that are derived from these products. Here, we present recent work on spectroscopy for the 0.76 mm O₂ A-band and the 1.61 and 2.06 mm CO₂ bands utilized by the NASA Orbiting Carbon Observatory missions (OCO-2 and OCO-3) and discuss future directions relevant for these and other greenhouse gas missions.

Efforts are underway to incorporate advanced line-shape formulations and to derive improved experimental line parameters. Advances in spectroscopy are included in the OCO forward model by updating look-up tables for molecular absorption coefficients (ABSCO tables). Recent updates to OCO ABSCO tables include results from a new multispectrum analysis of O₂ spectra acquired over a wide range of temperature and pressure, where details of the line-shape profile, the extent of line-mixing and the collision-induced absorption were determined in a self-consistent model [Drouin et al., 2017]. Updates also include results of new multispectrum analyses of the 1.61 mm and 2.06 mm CO₂ bands with improved constraints on the temperature dependence for these bands [Devi et al., 2016; Benner et al. 2016]. We present results of validation of these spectroscopic updates using ground-based atmospheric spectra and retrievals from the Total Carbon Column Observing Network (TCCON) site in Lamont, Oklahoma [Oyafuso et al., 2017] as well as satellite-based spectra and retrievals from OCO-2. In addition to showing the reduction in residuals and retrieval biases associated with the updates, we will discuss outstanding issues and potential paths to resolving these.

Odorants and Broadband Rotational Spectroscopy: What can we learn?

Maria Eugenia Sanz

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Our sense of smell is usually referred to as the least known among all our senses. Several theories have been proposed over the years trying to explain how we smell but none of them provide a comprehensive understanding of the fundamentals of olfaction. Detailed information on how the interactions between odorants and olfactory receptors occur at the molecular level is still lacking. To achieve a better understanding on the molecular mechanisms involved in olfaction, we are investigating several odorants and their interactions with water and mimics of amino acid residues in olfactory receptors using broadband rotational spectroscopy. In this talk we will present an overview of our recent work on odorants and their clusters. Our results provide information on the intra- and intermolecular interactions determining structure and conformation, and highlight the relevant role of secondary interactions.

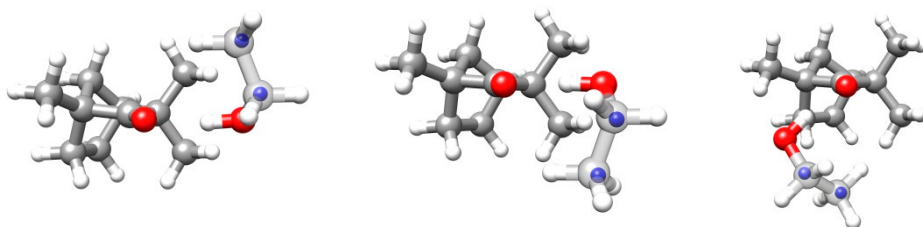


Figure 1. Observed conformers of the fenchone–ethanol complex.

Joyful Pursuit of Molecular Dynamics and Spectra

Dudley R. Herschbach

Harvard University, USA

This talk will hark back 60 years, to my graduate student days using microwave spectroscopy, and then look ahead to current prophetic excursions, using intense laser spectroscopy. My Ph.D. mentor, E. Bright Wilson, was a superb scientist and mentor. In the mid-1950s, his lab was focused on rotational spectra perturbed by hindered internal torsion of a methyl group on asymmetric top molecules. A major part of my thesis was devoted to propylene oxide, chosen as ideal to test theory dealing with the three-fold barrier for methyl torsion, which induces tunneling among the rotational levels. With Jerry Swalen, we measured spectra over a very large range of rotational lines ($J = 1$ to 48, $K = 1$ –25) and found dramatic splittings due to tunneling, confirming theory.

Another happy episode dealt with the equilibrium conformation of propylene. With Larry Krisher, we were curious whether one of the methyl hydrogens is eclipsed with respect to the double bond. To find out, we had fun making a sample of $\text{CH}_2\text{DCH}=\text{CH}_2$. In just a few hours, we had confirmed the expected two distinct rotational isomers: one had D eclipse the double bond, the other had D staggered. Thirty years later, I was astonished by a talk by Yoshi Kishi. He reported an epic synthesis of palytoxin, $\text{C}_{129}\text{H}_{223}\text{N}_3\text{O}_{54}$, a molecule with $2^{72} = 5 \times 10^{21}$ distinct stereoisomers. Kishi achieved, in 8-years, the exact stereoisomer he wanted—the biologically active neurotoxin. He had devised a key steric tool, by knowing the propylene conformation.

This month, with Qi Wei, Sabre Kais, and Tomokazu Yasuike, we have sent off a theoretical paper titled “Molecular binding induced by intense laser fields: helium dimer, pendular states, and strong chemical bonds.” We treat two pulsed laser realms: (I) Fields not strong enough to dislodge electrons, but interact with the anisotropic *polarizability* to induce spatial alignment of the molecular axis. (II) Superintense, high-frequency lasers that impel electrons to undergo *quiver oscillations* which interact with the intrinsic Coulomb forces and induce an extremely strong chemical bond. By including in (II) an excited electronic state, we bring out features amenable to experimental spectroscopy.

Correlated Rotational Alignment Spectroscopy: High-Resolution, Absolute Frequency Spectroscopy in the Time Domain

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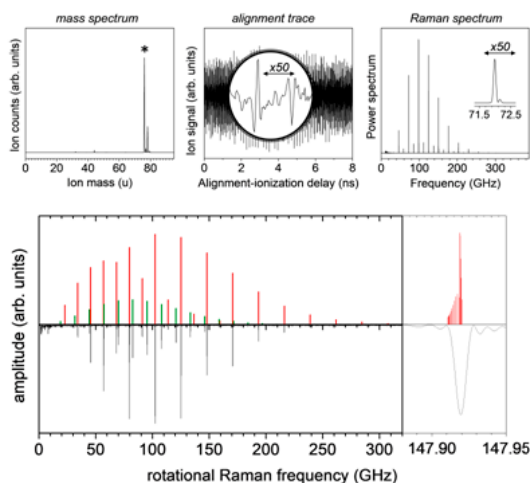
We describe the measurement of absolute frequency, high-resolution, broad-bandwidth rotational Raman spectra that are correlated with molecular mass. The Raman spectra have order-of-magnitude higher resolution as compared to preceding literature data. Rotational constants were determined with single-kHz accuracy, competitive with uncorrelated high-resolution Fourier-transform microwave experiments.

The experiment is based on correlated rotational alignment spectroscopy (CRASY, [1]): A femtosecond 'alignment' laser pulse excites a coherent rotational wave packet in a cold molecular beam. The wave packet evolution is probed by resonant multi-photon ionization with a second laser pulse, followed by ion detection in a mass spectrometer. Figure 1 shows resulting data: A mass spectrum of a carbon disulfide sample shows multiple isotopes (76 u to 82 u) and fragments (12 u to 66 u). Scanning of the alignment-ionization delay reveals signal modulations in each mass channel, as plotted for mass 76 u in the alignment trace. Fourier transformation of the alignment trace gives a rotational Raman spectrum for the selected mass. Insets show signals with 50-fold enlarged abscissa.

The spectroscopic resolution and bandwidth is determined by the range and step size of probed time-delays. A 1 picosecond step-size (0.5 THz spectroscopic bandwidth) was sufficient to resolve the complete rotational spectrum of carbon disulfide in a cold molecular beam. A delay range up to few nanoseconds can be scanned by opto-mechanical delays (moving mirrors on a motorized stage), leading to resolutions in the 100 MHz range (cf. Fig. 1).

We exploited the discrete time-domain property of the 80 MHz Ti:Sa laser oscillator pulse train to increase the spectroscopic resolution and accuracy. Pulse-selection for alignment and ionization pulses added discrete $(80 \text{ MHz})^{-1} = 12.5 \text{ ns}$ delays and extended the delay range to the sub-microsecond regime (few-MHz resolution). A simple measurement of the oscillator repetition rate tied measured spectroscopic frequencies to a reference clock, creating a time-domain equivalent to frequency comb spectroscopy. Spectroscopic data for carbon disulfide allowed to determine rotational constants with kHz accuracy for multiple isotopologues [2].

Figure 2 shows unpublished data for a mixture of carbon disulfide and benzene. The spectrum (bottom) at mass 78 u is compared to the best PGOPHER fit (top) for the main benzene isotopologue (red) and the rare $^{32}\text{S}^{12}\text{C}^{34}\text{S}$ isotopologue (green). The right hand side shows a small section of a non-apodized higher-resolution (11 MHz) measurement.



- [1] Schröter C., Kosma K., Schultz T., Crasy: Mass- or electron-correlated rotational alignment spectroscopy. *Science* **333**, 1011–1015 (2011).
- [2] Schroter, C., Lee, J. C., Schultz, T., Mass-Correlated Rotational Raman Spectra with High Resolution, Broad Bandwidth, and Absolute Frequency Accuracy. *PNAS* **115**, 5072 (2018).

Space exploration of Venus, Mars and beyond using (relatively) high resolution spectroscopy

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PT8

Mars has been monitored for decades now, either from Earth using large telescopes and sensitive spectrometers, from the Hubble Space Telescope, from rovers or platforms on the surface of Mars and of course from instruments in orbit around the planet. The last atmospheric mission to Mars, the ESA/ROSCOSMOS ExoMars Trace Gas Orbiter, launched in 2016, just started its Science phase in April 2018. On board, two spectrometers' suites will probe the atmosphere covering the UV to IR range. The Venus Express mission observed the atmosphere of Venus down to its surface with a wide range of spectrometers. Cassini-Huygens probed the Saturnine system with UV and IR instruments, while Juno is observing Jupiter. New missions are being prepared to go back to Venus or to the moons of Jupiter. Ground-based and space telescopes in Earth orbit are also being improved or built, providing us with spectra of a wide variety of objects. The James Webb Space Telescope will (soon) replace the Hubble Space Telescope, although its launch has again been postponed. Missions to observe exoplanets are being prepared, with CHEOPS to be launched in 2018, followed by PLATO and ARIEL. I will review the capabilities in terms of spectral coverage and resolution of these space missions and instruments on board, showing that although their resolutions might not be as high as spectroscopists might wish, they allow for very interesting science.

Nature and Strength of Unconventional Hydrogen Bonds

P19.

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Intermolecular interaction involving hydrides of the most electronegative elements such O, N, halogens and electron rich atoms or group of atoms of neighboring molecules has been termed and widely accepted as hydrogen bonding interaction. In the traditional definition of the conventional H-bond the most highlighted part is that in the $XH\cdots Y$ type of interactions both X and Y must be highly electronegative. There had been, however, reluctance to accept the interactions involving hydrides of lesser electronegative elements such as carbon, sulfur, selenium as H-bonding interactions. In early days classifying such interactions as H-bonding was based on the bond distance criteria obtained from the crystallographic database, and to a limited extent on the NMR and IR data due to lack of any other spectroscopic data and was heavily contested at times. The most celebrated case has been the CH-Y interaction.

In the last couple of decades a significant progress has been made in regard to obtaining the spectroscopic data on weak hydrogen bonding interactions in an isolated condition of gas phase. Our group has been working on characterization of several unconventional hydrogen bonds. The adjective *unconventional* is used to differentiate the $XH\cdots Y$ hydrogen bonds that do not involve strongly electronegative X or Y atoms or group of atoms. The emphasis has been on the sulfur centered hydrogen bonds and $CH\cdots Y$ type hydrogen bonds. In this talk I will present our spectroscopic results on the selected examples of both types. We show that the sulfur centered H-bonding interaction is dominated by the dispersion interaction besides showing all the characteristics of conventional hydrogen bond. In the case of $CH\cdots Y$ type hydrogen bonds I will show examples of red, blue, and zero shift hydrogen bonds. I will also show that the $CH\cdots Y$ hydrogen bonds also exhibit all the characteristics of conventional proper hydrogen bonds and there is nothing improper about it.

High resolution spectra of floppy molecules: neutral and ionic species

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Recent progress in the experimental technique in spectroscopy, i.e. in resolution, precision, and sensitivity, makes it possible to investigate the static and dynamic behavior of molecules in detail. Consequently, or better to say surprisingly, we are facing now a variety of difficulties to explain the observed phenomena due to the large amplitude motions involved. Very often, they are not easy to be handled by the standard theory which have been developed with the assumptions of small amplitude vibration.

In this lecture several results for HOOD [1], C_3 [2], and CH_5^+ [3] will be presented, as well as some newly investigated ionic species. The spectra of neutral species have been observed and analyzed recently by the spectroscopy group of Kassel university, and those of ionic species by the group of Cologne University.

Hydrogen peroxide is a classical example of the molecule with a large amplitude motion (i.e. internal rotation or torsion). Although the spectra of HOOH and DOOD have been investigated in detail and we understand the structure including the torsional potential, for the remaining isotopologue, HOOD, details were not known for long years. In the last decade we have measured and assigned the FIR and THz spectra in Kassel [1]. In the study we found accidental resonances between the tunnel doublets in the lowest K_a levels, which blocked the assignment for long years.

The C_3 radical is also known as a molecule with a large amplitude motion. Recently the THz spectra of the bending fundamental (ν_2) band was successfully measured and analyzed in Kassel [2]. In the course of structure determination, we found that the moment of inertia along the molecular axis I_z may not be zero in average in the ground vibrational state although it should vanish in the r_e structure.

High resolution IR and THz spectroscopy of ions trapped in a cryogenic ion trap has been developed by Schlemmer and coworkers in Cologne. By using the trap, they have been very successful in observing numerous ionic species, of rigid or non-rigid structure. The awfully complicated spectra of CH_5^+ were measured in IR and we have published a paper in 2015 [3], where several combination differences for the ground vibrational state are reported, without proper assignments.

It would need still many years, or decades, to tame these *enfant terribles* in spectroscopy including the CH_5^+ ion.

- [1] D. Herberth, O. Baum, O. Pirali, P. Roy, S. Thorwirth, K. M. T. Yamada, S. Schlemmer and T. F. Giesen, *J. Quant. Spectrosc. Radiat. Transfer*, **113**, 1117–1133 (2012).
- [2] A. A. Breier, T. Büchling, R. Schnierer, Volker Lutter, G. W. Fuchs, K. M. T. Yamada, B. Mookerjee, J. Stutzki, and T. F. Giesen, *J. Chem. Phys.* **145**, 234302:1–10 (2016).
- [3] O. Asvany, K. M. T. Yamada, S. Brünken, A. Potapov, and S. Schlemmer, *Science*, **347**, 1346–1349 (2015).

Oral Sessions

In the following pages all conference abstracts have been ordered by day and session.

The abstract numbers correspond to the daily scientific program in page 12.

You can search for specific authors in the author index at the end of this abstract book (all authors and co-authors are listed in alphabetical order with their abstract number/s).

Microwave study of internal rotation in *para* Tolualdehyde: local versus global symmetry at the methyl-rotor site as an indicator of information transfer across the benzene ring

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The rotational spectrum of *para*-tolualdehyde ($\text{CH}_3\text{-C}_6\text{H}_4\text{-CHO}$) has been measured using microwave spectrometers in three laboratories, with the goal of quantifying the influence of the aldehyde group at the top of the benzene ring on the internal rotation barrier seen by the methyl group at the bottom of the ring. This barrier consists of a six-fold component, which results from the local C_{2v} symmetry of the benzene ring seen by the methyl top (as in toluene), and an additional three-fold component, which results from information on the non- C_{2v} symmetry at the aldehyde site being transmitted across the ring to the methyl top site.

The nearly free internal rotation of the methyl group splits each of the rotational transitions into two components, one of *A* and one of *E* symmetry. Assignment and fit of 786 *A*-state and *E*-state transitions in the $\nu_t = 0, 1$, and 2 torsional levels to an internal rotation Hamiltonian with centrifugal distortion and barrier terms of three-fold ($V_3 = 28.111(1) \text{ cm}^{-1}$) and six-fold ($V_6 = -4.768(7) \text{ cm}^{-1}$) symmetry with respect to the internal rotation angle, resulted in residuals equal to experimental uncertainty. Isotopic data from all eight mono-substituted ^{13}C species and the one ^{18}O species were obtained in natural abundance and used to determine an r_s substitution structure.

Various chemical and physical implications of this structure and the two barriers will be discussed. In particular, our initial intuitive assumption that the information transmission mechanism would involve a conjugation of the n electrons of the aldehyde C=O with the n electrons of the benzene ring to force a partial Kekulé structure of the ring, is not supported by the substitution structure or quantum chemistry calculations. Other molecules potentially exhibiting this same type of information transfer across a conjugated aromatic ring system will be mentioned.

Effective rotational hamiltonian for two-rotor systems with symmetric and asymmetric internal rotors (like Ethanol) applied to Ethylphosphine, $\text{CH}_3\text{CH}_2\text{PH}_2$

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Spectra of molecules with a 3-fold internal rotor become much more interesting in the presence of another large-amplitude motion (LAM) that leads to tunneling between equivalent asymmetric forms which may also tunnel to a different conformer. An effective rotational Hamiltonian has been derived for such a system of which ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, is a typical example [1]. The ERHAM code [2] was modified to treat ethanol-type systems, using “ancient” unpublished microwave data from vibrational ground and excited states of ethylphosphine, $\text{CH}_3\text{CH}_2\text{PH}_2$, as test data. For gauche ethylphosphine, the splitting between the a-type Coriolis-coupled ground states is 5.215(6) MHz whereas it is 229.9(2) MHz in the ν_{24} state (PH_2 torsion) and 51.35(7) MHz in the ν_{23} state (CH_3 torsion). The tunneling energy coefficients eps_{01} for the methyl internal rotation are -0.63(2) MHz and 2.93(5) MHz (sign undeterminable), respectively. These results look promising; however, up to now, sets of assigned frequencies had to be omitted from fits to experimental uncertainty of 25 kHz: (a) for the ground state, all c-type transitions $J_{4J-3} - J_{3J-3}$ ($41 < J < 48$) for systematic large deviations (reason unknown); (b) for the ν_{24} state, half of the quartets of the $J_{3J-2} - J_{2J-2}$ series ($28 < J < 32$) because of interactions with a state of the trans conformer) and some of the $K_a = 1, 2$ low- J transitions (incorrect assignments or unknown reasons).

[1] J.C. Pearson et al., J. Mol. Spectrosc. (2008) 251, 394

[2] P. Groner, J. Mol. Spectrosc. (2012) 278, 52

Proton in a double-well potential: Acetylacetone and its derivatives by microwave spectroscopy

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The extended nature of the proton wave function, the shape of the ground and final state potentials in which the proton is located has been investigated in gaseous acetylacetone and three of its derivatives, benzoylacetone, dibenzoylmethane [1] and 3,5-heptanedione by quantum chemical calculations, microwave spectroscopy and core level photoemission study. These molecules show intramolecular hydrogen bonds, in which a proton is located in a double well potential, whose barrier height is different for the four compounds, allowing us to examine the effect of the shape of double well on photoemission and rotational spectra. For all of them, two distinct O 1s core hole peaks are observed, previously assigned to two chemical states of oxygen in the ground state. We provide an alternative assignment by taking full account of the finite temperature of the samples based on quantum chemical calculations and symmetry consideration.

A13.

[1] J. Phys. Chem. Lett. 2018, 9, 521.

Sensing the molecular structures of alkyl methyl ketones by internal rotation in the microwave spectrum

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Predicting and understanding the barriers to internal rotation in ketones is a difficult task, even with the assistance of modern quantum chemical methods. Previous studies on ketones containing an acetyl methyl group as an internal rotor have shown that the barrier height ranges from about 170 cm^{-1} to 440 cm^{-1} apparently without any trend. In the present work, we systematically recorded a series of alkyl methyl ketones, which are (a) pentan-2-one, (b) hexan-2-one, (c) heptan-2-one and (d) octan-2-one (see Figure 1), using pulsed molecular jet Fourier transform microwave spectrometers operating in the frequency range of 2 – 40 GHz. All spectra exhibit torsional splittings due to internal rotation of the acetyl methyl group and they were fitted to measurement accuracy with the programs XIAM and BELGI.

For each molecule, at least two conformers could be identified in the spectrum. The first conformer type features a straight alkyl chain and an acetyl methyl barrier height of $185 \pm 3 \text{ cm}^{-1}$. In case of the second kind of conformers the alkyl chain is bent with the γ -carbon (the third carbon atom of the alkyl chain counted from the carbonyl group) in a synclinal position. Here, the barrier height is $235 \pm 3 \text{ cm}^{-1}$. In addition, a third conformer with a barrier value of 182 cm^{-1} was found for hexan-2-one. In this conformer, the δ -carbon of the alkyl chain is located in a synclinal position.

These observations allow to link the experimentally deduced barrier heights with the positions of the γ -carbon and thus to establish a first rule to predict the barrier heights of acetyl methyl groups in ketones: If the γ -carbon of an alkyl methyl ketones is located in the C-(C=O)-C plane, the barrier height is about 185 cm^{-1} . If the γ -carbon position is synclinal, a barrier of approximately 235 cm^{-1} is observed.

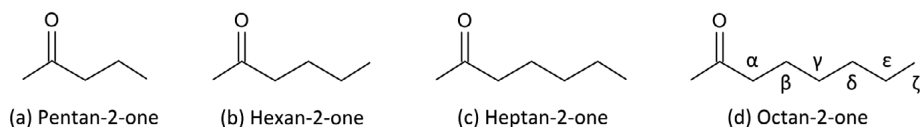


Figure 1: Systematic investigations on alkyl methyl ketones.

Structures and dynamics of acrolein-(H₂O)_n clusters revealed by MW spectroscopy and *ab initio* calculation

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1) University of Bologna

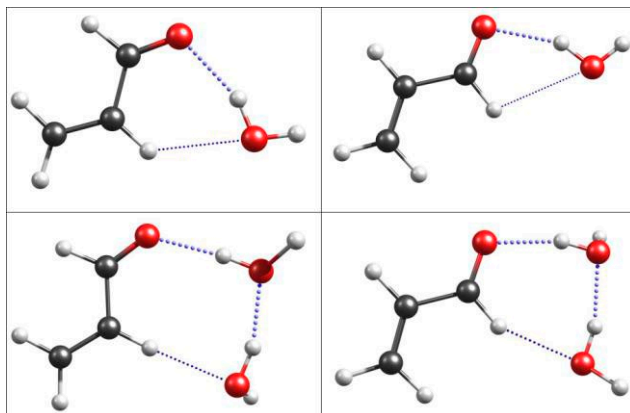
2) Universidad del País Vasco (UPV-EHU)

3) Stockholm University

We present a rotational study of the interaction between the simplest unsaturated aldehyde Acrolein (ACR) and water (W) by using cavity based coaxial pulsed jet Fourier transform microwave spectroscopy. The rotational spectra of two conformers of the dimer ACR-W and two conformers of the trimer ACR-W₂ were identified in the frequency range 6.5–18.5 GHz.^[1]

Acrolein is present only as *trans* isomer in all the assigned clusters which agrees with the preference of *ab initio* predictions. ACR is linked with one or two water molecules through the OH...O hydrogen bond (HB) and the C_αH...O/C_βH...O weak HB.

The ¹³C and ¹⁸O monosubstituted isotopologues of ACR-W and the ¹⁸O species of A-W₂ have been also assigned. The spectroscopy intensity of the clusters including acrolein-¹⁸O increased dramatically when we seeded normal acrolein and H₂¹⁸O in the sample. This implies that the exchange of the O atoms between acrolein and water happened. The *ab initio* calculation helped us to explore the reaction pathways.



Discovering the conformations of formamide complexes and formamide–water clusters by microwave spectroscopy

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B12.

We have recorded the broadband microwave spectra (2–8 GHz) of pure formamide (¹⁴N and ¹⁵N isotopologues) and mixtures of formamide and water using a chirped-pulse Fourier transform microwave spectrometer. The structures of several clusters of the formamide trimer have been identified using the rotational parameters determined for the different isotopologues detected. In the formamide–water spectra, two complexes, F–(H₂O)₄ and F₂–(H₂O)₂, have been identified from the rotational and quadrupole coupling constants. We present the predicted conformational landscape of complexes and the preliminary results obtained.

Does the structure of the polycyclic aromatic hydrocarbon impact the aggregation of water on its surface? Fluorene vs acenaphthene

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2) Deutsches Elektronen-Synchrotron (DESY), Hamburg

3) Facultad de Ciencia y Tecnología, Universidad del País Vasco, Leioa

4) Department of Chemistry, Furman University, Greenville, SC

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Polycyclic aromatic hydrocarbons (PAHs) are thought to be ubiquitous in the interstellar medium, and as such they would play a key role in everything from complex organic molecule formation to the formation of ice grains. In the event of ice grain formation, PAH-water interactions would be of importance. In this investigation we aim to study the onset of these interactions using chirped pulse Fourier transform microwave (CP-FTMW) spectroscopy. Fluorene, which was previously studied [1], and its complexes with water were measured. Transitions for ^{13}C species of the monomer were observed, as well as the ^{18}O isotopologues of the water complexes. This allowed for the structural analysis of the species to be performed. These structures will be compared to the previously studied acenaphthene (Ace) and $\text{Ace}-(\text{H}_2\text{O})_n$ ($n=1-4$) [2]. As in the Ace-water study, we have observed up to three water molecules complexed with fluorene. In this talk we will present these findings and the structural differences between the two PAH-water systems.

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[2] Steber, A.L., Pérez, C., Temelso, B., Shields, G.C., Rijs, A.M., Pate, B.H., Kisiel, Z., Schnell, M. *J. Phys. Chem. Lett.*, 2017, 8, 5744.

Characterization of microsolvated 15C5 crown ether from broadband rotational spectroscopy

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B14.

15-crown-5 ether (15C5) and its complexes with water generated in a supersonic jet have been studied using broadband Fourier transform microwave spectroscopy. The most stable form of the crown ether not previously reported, to complete a total of nine isolated forms, has been detected. In addition, two 1:1 and two 1:2 clusters have been observed. The clusters structures have been unambiguously identified through the observation of water ¹⁸O isotopologue spectra and a detailed analysis of the rotational parameters. The structures of all the clusters show that at least one water molecule, located close to the axis of the ring, interacts through two simultaneous hydrogen bonds to the endocyclic oxygen atoms. This interaction reshapes the 15C5 ring to reduce its rich conformational panorama to only two open structures, related to those found in complexes with Li⁺ or Na⁺ ions. In the most intense 1:2 form, the two water molecules repeat the same interaction scheme in both sides of the ring while in the second one the water molecules lie on the same side of the ring.

Fast scanning IR-spectrometer to measure transient molecules in a pulsed supersonic jet

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¹) *University of Kassel*

Continuous wave (cw) narrow bandwidth Quantum Cascade lasers (QCL) with enhanced output powers (50–100 mW) and with large tuning ranges at infrared wavelengths (1–20 μm) allow for new spectroscopic applications. Fast IR-detector systems of up to 1 GHz response time became commercially available, enabling fast scanning and fast recording techniques. We have used a QCL-spectrometer at 10 μm to record spectra of transient molecules formed in a pulsed supersonic jet.

The molecules were produced by laser ablation of a target rod (e.g. aluminum or titanium) with the addition of a gaseous oxygen donor (O_2 or N_2O). The pulsed Nd:YAG laser ablation source produces molecular absorption signals of 10 μs duration time and with 20 Hz repetition rate. Scanning the infrared laser frequency at a tuning rate of 100 kHz allows the recording of the complete spectrum within 10 μs . At 1 GHz detector bandwidth the sample recording speed is set to 10 000 samples per scan (1 GS/s). A fast digitizer is used to store the spectra in a computer where single spectra are automatically calibrated and co-added in order to significantly improve the signal-to-noise ratio.

We used the new fast scanning spectrometer to record spectra in the 10 μm region of titanium monoxide (TiO). These TiO data, but also other infrared spectra of molecules formed from refractory elements (e.g., Al, Fe, C, Si), can be used for possible future astronomical observations of these species in the dust forming regions of late-type stars. The new generation of high resolution IR instruments (e.g. EXES/SOFIA or TEXES/Gemini North) with spectral resolution of 100 000 will allow to record spectra of small dust forming molecules and will give new insights to the fundamental processes leading to stellar dust formation. Despite their high importance, laboratory data of these molecules are still rather sparse to date.

Wide bandwidth mid-IR spectroscopy with comb-referenced EC-QCL: application to the ν_1 fundamental band of $^{14}\text{N}_2^{16}\text{O}$

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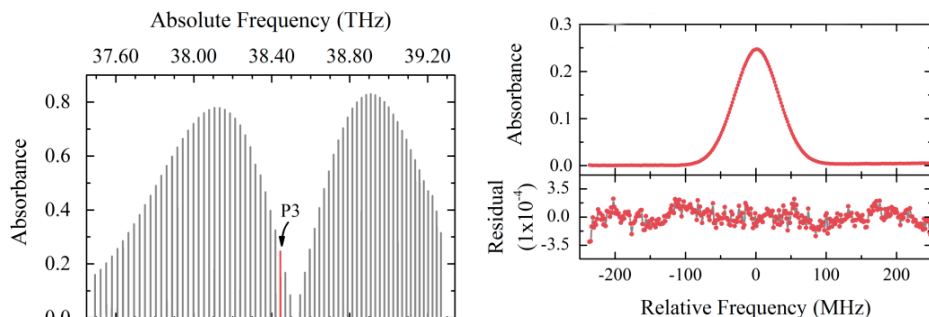
C12.

Molecular line parameters collected in spectroscopic databases such as HITRAN are mainly retrieved from Fourier Transform spectroscopy with uncertainties that cannot overcome the MHz level. An improvement of four orders of magnitude is possible employing optical frequency combs to calibrate the frequency axis of a probe laser. In the extremely interesting spectral region of mid-ir, the only laser source suitable for wideband spectroscopy is represented by extended cavity quantum cascade lasers (EC-QCLs) with tunability that could exceed 100 cm^{-1} . Unfortunately, these lasers suffer from a large amount of frequency noise [1] preventing the possibility to lock it against a frequency comb synthesizer.

In this work we overcome this limitation and describe a spectrometer that relies for the first time on the frequency locking of an EC-QCL tunable in the $1217\text{--}1328\text{ cm}^{-1}$ range to a $1.9\text{ }\mu\text{m}$ Tm: Fiber comb exploiting a sum frequency generation scheme [2].

It is applied to the first comb-calibrated direct characterisation of the ν_1 fundamental band of N_2O , specifically of nearly 70 lines in the $1240\text{--}1310\text{ cm}^{-1}$ range, from P(40) to R(31) [3]. An overview of the measurements is presented in Fig. 1. Each line results from the average of 10 spectra acquired in 6 minutes at slightly different pressures, from 0.01 to 0.04 mbar. Such low-pressure regime allows to use a Gaussian profile for the fitting. Fig. 2 reports a 10-times averaged spectrum of the P(3) line together with the residuals. Line centers are retrieved with an uncertainty between 62 and 180 kHz.

The spectroscopic constants of the upper state are derived from a fit of the line centers with an average rms uncertainty of $4.8 \times 10^{-6}\text{ cm}^{-1}$ (144 kHz). The coupling of the spectrometer to a high-finesse optical cavity to the purpose of enhancing its sensitivity and addressing weaker absorbers, is also discussed.



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[3] J. Quant. Spectrosc. Radiat. Transfer 2018,211,172

Endless frequency-swept comb-calibrated spectrometer

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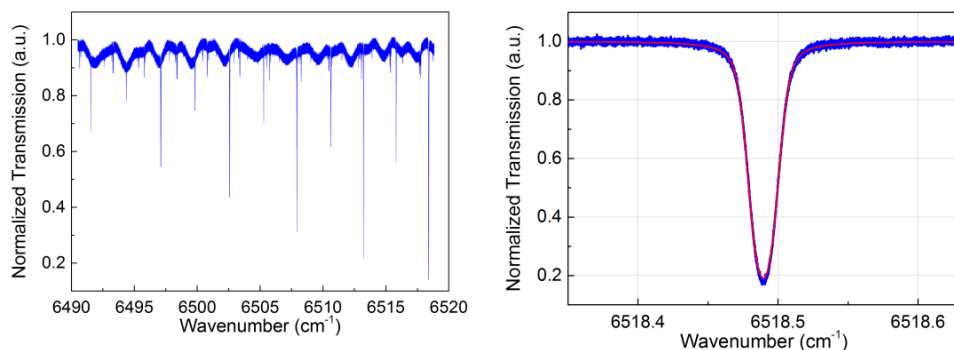
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The absolute frequency calibration afforded by optical frequency combs has enormously improved accuracy and comparability of spectroscopic measurements. Frequency combs are used either as a direct probe of molecular absorption, with the advantage of broad spectral coverage but at the price of spectral points separated by the comb repetition frequency, or in combination with a cw probe laser, which returns a very dense frequency axis and thus a high level of precision but in combination with speed and tuning range limitations given by the cw laser and/or by the referencing strategy.

Here we overcome these trade-offs by a new approach that bins the endless frequency shifting concept of an optical frequency comb proposed years ago by Rohde et al. [1] with the large and fast mode-hop-free tunability of a single-mode laser. Peculiarly, the laser remains phase-locked to the comb while being dragged by the comb itself over spectral ranges as large as a few THz at rates even beyond the THz/s.

As a proof-of-principle experiment, we measured the transmission spectrum of an acetylene cell in the range from 1533 to 1541 nm (about 1 THz in the frequency domain), encompassing 11 lines of the P-branch of the v_1+v_3 band. Figure 1 reports the normalized transmission spectrum acquired upon a frequency sweep of 400 GHz/s. The line centres retrieved from the fitting of the individual lines, as compared to HITRAN values, are affected by a statistical uncertainty of 1.5 MHz, which is remarkable if one considers a 2-ms scanning time per line and consistent with the current signal-to-noise-ratio of the measurement. Figure 2 reports the transmission spectrum of the 12P15 line (blue trace) together with the corresponding fitting profile (red trace). A line-by-line comparison between repeated sweeps does not show, at this level of precision, any bias, thus attesting a highly calibrated and repeatable frequency scan. A discussion about systematic and speed-dependent errors will be given together with preliminary results on the coupling of such system with a high-finesse optical cavity [2], in view of primary thermometry approaches and accurate testing of spectral line-shape models.



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Broadband complex gas spectroscopy with sub-kHz level resolution comb spectrometer

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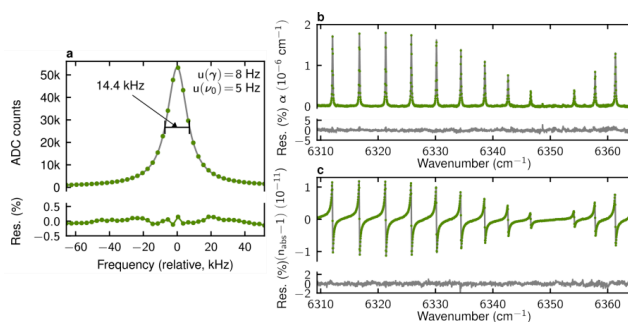
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Cavity mode-width spectroscopy [1] and cavity mode-dispersion spectroscopy [2] techniques provide a way to simultaneously determine absorption and dispersion of a sample by measuring widths and positions of enhancement cavity resonances. While these techniques were originally developed with continuous-wave lasers, they can also be efficiently combined with optical frequency combs (OFCs) [3,4]. We present broadband measurements of complex spectra of CO second overtone transitions, obtained from positions and widths of 7-kHz-wide cavity resonances determined at Hz-level precision. To the best of our knowledge, the cavity resonances shown in this work are the narrowest spectral features measured directly with a comb-based or non-comb-based broadband spectrometer. Moreover, the presented system is capable of retrieving shapes of such cavity modes in several seconds, enabling future ultra-precise, broadband and time-resolved spectroscopic measurements.

A near-infrared OFC with the repetition rate of 250 MHz is coupled into a high-finesse optical cavity ($F=18500$) and locked to the cavity modes. The controlled mismatch between the repetition rate of the OFC and the free spectral range of the cavity causes part of the comb to be filtered and produces a new OFC after the cavity with 4 GHz spacing between comb modes. The OFC is then transferred to a VIPA spectrograph with 600 MHz spectral resolution and 20 nm bandwidth to resolve the comb modes and retrieve their individual intensities. The shapes of the cavity modes are retrieved by measuring the transmitted spectrum as a function of the detuning of the OFC modes and the cavity modes.

Each cavity mode shape is fitted to a Lorentzian function (shown on Figure) to obtain its width and position. The mode widths and positions are converted to absorption coefficient and refractive index, respectively, and fitted to the complex Voigt profiles of probed transitions. We obtain signal-to-noise ratio of 190 for absorption spectrum and of 380 for dispersion spectrum with expected better performance for longer averaging times.

The research was supported by the National Science Center, Poland, project nos. 2015/18/E/ST2/00585, 2016/21/N/ST2/00334. G.K. was supported by the National Science Centre, Poland scholarship 2017/24/T/ST2/00242.



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Empirical potential energy surface and bending angle probability densities for the electronic ground state of HCO^+

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In molecular spectroscopy parlance, a linear molecule is defined as one whose potential energy minimum is at a linear geometry. The nature of the *average* structure of a linear triatomic molecule – linear or bent? – has given rise to much discussion recently. We contend that the average structure of a linear triatomic molecule is bent. The purpose of the present work is to underpin this argument with results from Coulomb Explosion Imaging (CEI) experiments for the linear DCO^+ ion [R. Wester et al., J. Chem. Phys., 2002, 116, 7000]; these experiments allow a direct experimental measurement of the bending angle probability density. We aim at simulating theoretically the CEI experiments for DCO^+ . The possibility of obtaining a detailed simulation is hampered by the fact that the DCO^+ ions investigated in the CEI experiment populate very highly excited vibrational states. This creates numerical problems for the theoretical calculations. We can conclude, however, that the results of the CEI experiment are in support of the average structure of a linear molecule being bent.

Torsion rotation program for nitromethane CH₃NO₂

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A2.2.

Nitromethane, CH₃NO₂, is the simplest representative of molecules with a C_{3v} symmetric top rotating relative to a C_{2v} frame. A very low six-fold barrier to internal rotation makes the torsional label *m* an almost good quantum number. The rotational quantum number *K_a* is much worse as a label because nitromethane is an asymmetric top closer to the oblate limit ($\kappa=0.25$). The PI symmetry group, G₁₂, is isomorphic to C_{6v} point group which possesses 6 irreducible symmetry species. However, a permutation of two oxygen atom ¹⁶O of nuclear spin equal to 0 allows only for a half of the species, namely A₁, A₂ and E₂. In the ground vibrational state the torsion-rotation functions must fulfill a strict condition $m+K_a = \text{even}$. If nitromethane is in a vibrational state of B₁, B₂ or E₁ the required condition is $m+K_a = \text{odd}$. Each torsion-rotation state is additionally labeled with *J* quantum number and a symmetry species in C_{6v} group.

The presented program allows for a determination of the condition “even or odd” for $m+K_a$. Furthermore, the torsion-rotation basis functions are derived using a full symmetry of G₁₂ group which results in relatively easy assignment of *m* and *K_a* as approximate labels to torsion-rotation energy levels. The Hamiltonian is similar to that used by Ilyushin [1] – it introduces the ρ constant which minimizes the torsion – rotation coupling and all interaction terms with $\cos 6\alpha$, $\sin 6\alpha$, $\cos 3\alpha$, $\sin 3\alpha$ functions. The detailed expressions will be shown.

This approach is closer to the Sørensen's program [2] than to the Ilyushin's approach [1] where *K_a* is no longer a label for the torsion-rotation states. On the other hand Sørensen did not use a full expansion on *m* but included limited interactions with neighboring torsional states in a range [*m*-6 to *m*+6]. The new program allows for calculation of transitions between different torsional states and facilitates determination of combination states where torsional transitions overlap a vibrational excitation.

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Weak intramolecular interaction effects on the structure and torsional spectra of ethylene glycol isotopologues, an astrophysical species

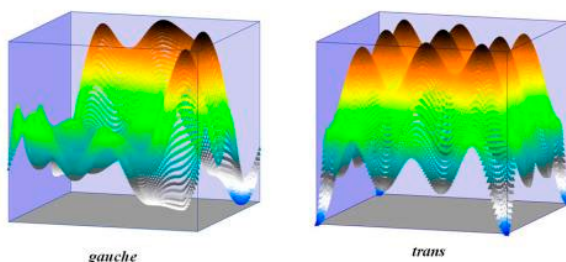
Rahma Boussessi¹, Maria Luisa Senent¹

1) IEM-CSIC

A2.3.

A variational procedure of reduced dimensionality based on CCSD(T)–F12 calculations is applied to understand the far infrared spectrum of various isotopologues of Ethylene–Glycol [1] a detected molecule in gas phase [2]. This molecule can be classified in the double molecular symmetry group G_8 and displays nine stable conformers, *gauche* and *trans*. In the *gauche* region, the effect of the potential energy surface anisotropy due to the formation of intramolecular hydrogen bonds is relevant. For the primary conformer, the ground vibrational state rotational constants of the main isotopologue are computed at 6.3 MHz, 7.2 MHz and 3.5 MHz from the experimental parameters [3].

Ethylene glycol displays very low torsional energy levels whose classification is not straightforward. Given the anisotropy, tunneling splittings are significant and unpredictable. The ground vibrational state splits into 16 sublevels separated $\sim 142\text{ cm}^{-1}$. Transitions corresponding to the three internal rotation modes allow assign previous observed Q branches. Band patterns, calculated between 362.3 cm^{-1} and 375.2 cm^{-1} , between 504 cm^{-1} and 517 cm^{-1} and between 223.3 cm^{-1} and 224.1 cm^{-1} , that correspond to the tunnelling components of the ν_{21} fundamental ($\nu_{21} = \text{OH-torsional mode}$), are assigned to the prominent experimental Q branches [1]. Isotopic displacements of the bands can help assignments.



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Modelling temperature dependent anharmonic spectra of pyrene (C₁₆H₁₀): comparison of computational approaches

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A2.4.

Polycyclic Aromatic Hydrocarbons (PAHs) are believed to be responsible for the Aromatic Infrared Bands (AIBs) observed in many astronomical objects [1]. The excitation mechanism involves the absorption of an UV photon via an electronic transition and a sequence of radiationless transitions converting most of the absorbed energy into vibrational excitation in the electronic ground state [2].

The hot molecule then relaxes by emitting IR photons, the resulting spectrum being dominated by many hot bands, all slightly shifted with respect to the corresponding 1→0 fundamentals due to anharmonicity. IR spectra of PAHs are usually computed at OK either by scaled harmonic or by 2nd order perturbation theory but none of them describes the thermal behavior of the bands.

We used the new AnharmoniCaOs code [3] to compute the temperature dependent IR spectra of pyrene (C₁₆H₁₀). After identifying resonance terms, we iteratively construct the polyad and solve the effective Hamiltonian. Monte Carlo sampling of the vibrational states up to 12000 cm⁻¹ is used to obtain the temperature dependent spectra up to 600K. Our code works efficiently at low and moderately high temperature but due to high computational cost it is very expensive to extend it to higher temperature, relevant for astrophysics. This calls for methods based on classical molecular dynamics (MD) simulations, albeit at the cost of losing all information on the detailed structure of hot bands. We calculated the potential energy surface using the Density Functional based tight binding (DFTB) method [4] as available in the deMonNano code [5]. Finite temperature IR spectra are then derived from MD trajectories, computing the Fourier transform of the autocorrelation function of the dipole moment [6].

We report here more specifically on different characteristics of the temperature-dependent IR spectrum including band position and width with temperature. We compare the results from both computational methods and with experimental data [7, 8]. Considerations on the weak and strong points of each method are provided.

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Non-adiabatic coupling in the ozone molecule

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The question whether a Berry phase should be included in the calculation of rovibronic states of the ozone molecule in its electronic ground state has been addressed in the present work [1]. Since several conical intersections connect the three lowest singlet states, a phase of π generated by a symmetry-demanded conical intersection between states 2 and 3 might be present, or it might be compensated by further conical intersections. Hyperspherical coordinates were employed here as they provide a natural choice for the cyclic coordinate that is needed to investigate the presence or absence of such a topological phase. On a hyperspherical grid, we have computed the electronic energies of the three lowest singlet states using a multi-reference configuration interaction (MRCI) procedure. Non-adiabatic coupling terms along the cyclic variable were evaluated numerically. Investigation of the behaviour of the adiabatic-to-diabatic transformation angles, using the quantization criterion of the non-adiabatic coupling terms (Baer and Alijah, Chem. Phys. Lett. 319, 489 (2000)), shows that a geometrical phase is retained. This phase has no practical effect on the well-established energy values of the rovibrational states located deeply in the three equivalent C_{2v} potential wells, but will come into action as highly excited states reach the dissociation region.

A2.5.

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The long-range behavior of ab initio transition dipole moments and spin-orbit coupling matrix elements between the low-lying electronic states of alkali heterodimers

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A2.6.

Often times the most efficient laser cooling pathways require the use of weakly bound states close to the dissociation limits as intermediate steps. The exact singlet/triplet composition of these states as well as their exact energies and radiative properties must therefore be known in advance with high precision and accuracy. Unfortunately, these states are heavily influenced both by the exact shape of the potential energy curve (PEC) and by the asymptotic behavior of the spin allowed transition dipole moments (TDMs) and spin-orbit coupling (SOC) matrix elements. Thus, having correct long range TDM and SOC functions, together with the relevant PECs [1,2], could be applied to the comprehensive coupled-channel (CC) treatment of the competitive radiative and predissociative dynamics of the mutually perturbed rovibronic states located in the vicinity of dissociation thresholds

The asymptotic behavior of spin allowed TDMs and SOC matrix elements between electronic states converging to the lowest three dissociation limits were investigated for the lightest heteronuclear alkali diatomics XY ($X, Y = \{\text{Li, Na, K, Rb}\}$). The TDM and SOC functions are evaluated in the basis of the spin-averaged wavefunctions corresponding to pure Hund's coupling case (a) by means of effective core pseudopotentials. The electronic correlation is accounted for by applying the multi-reference configuration interaction method to only two valence electrons for all considered molecules and core-polarization potentials are used to take the core-valence effect into account.

In this work, the leading asymptotic behavior of the TDM and SOC functions has been found to be R^{-3} and R^{-6} . Additionally, in the case of the TDM functions, our ab initio results [3] have been found to coincide with their analytical counterparts obtained within the framework of the long-range perturbation theory by Chu and Dalgarno [4].

The study was funded by RFBR according to the bilateral Russia-Bulgaria research project 17-53-18006.

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FTMW spectroscopy of sulfur bearing free radicals, HCSC and CH₃SS

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Two new sulfur bearing free radicals, HCSC and CH₃SS, were observed in a discharged plasma containing CH₃SH diluted in Ar, using a Balle-Flygare type Fourier transform microwave spectrometer together with a MW-MW double resonance setup. The HCSC radical is a high energy isomer of well known free radical, HCCS, about 100 kcal/mol higher in energy. Fairly strong lines with fine and hyperfine splittings were observed slightly below 16 GHz, which were assigned to $N=1-0$, with the $^2\Sigma$ pattern indicating that this radical is bent, while HCCS is linear. The observation was extended to transitions with $N=3-2$ using double resonance. So far only $K_a=0$ transitions were observed. Although the signals of HCSC were strong with the present precursor, those of HCCS were very weak.

In addition to the lines of HCSC, lines with very complicated splittings were observed extending in the region 16 GHz to 18 GHz, which were finally assigned to transitions of CH₃SS. The CH₃SS radical has a bent CSS structure with internal rotation of the methyl top. Thus, this species consists of a series of open shell radicals, CH₃OO, CH₃SO, and CH₃SS, where FTMW spectra have been observed for the former two species (K. Kato *et al.*, unpublished). A number of lines have been observed with N_{up} to 4 with $K_a=0$ and 1, for a - and b -type transitions. Splittings due the spin-rotation interaction, the proton hyperfine interaction, and the A/E splittings due to internal rotation of the methyl top have been observed for this species, which were analyzed by the Hamiltonian for open shell species with internal rotation. The present data together with those of CH₃OO and CH₃SO may provide invaluable data for deeper understanding of the energy levels of open shell species with internal rotation, which have not been studied well so far.

Millimeter-wave spectroscopy of the HDCCH radical

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B2.2

The vinyl radical, H_2CCH , has a proton tunneling motion of α -proton governed by a double minimum potential with barrier height of 1580 cm^{-1} [1]. The ground state splits into a doublet (0^+ and 0^-) and the proton tunneling transitions between the 0^+ and 0^- levels have been observed by MMW spectroscopy[1, 2]. If one of the b -proton is deuterated, the effective 1-D potential for the α -proton bending motion becomes to be asymmetric due to the zero point vibrations of b -deuteron. The proton tunneling is hindered and the b -type rotational transitions of $\Delta K_a = \pm 1$ will be observed within the *cis*- and *trans*-tautomers instead of the tunneling transition, where *cis*-HDCCH has an unpaired electron on the same side of deuterium with respect to the C=C double bond, while *trans*-HDCCH on the opposite side.

In the present study, the HDCCH radical produced by the 193 nm excimer laser photolysis of HDCCHCl have been observed by MMW spectroscopy combined with a pulsed supersonic jet technique. The b -type rotational transitions of $N_{K_a, K_c} = 1_{11} - 0_{00}$, $2_{12} - 1_{01}$, $1_{10} - 1_{01}$, and $2_{11} - 2_{02}$ as well as the a -type transitions of $2_{02} - 1_{01}$ and $3_{03} - 2_{02}$ were observed for one tautomer in the frequency region of 100 – 260 GHz.

Observed A_0 rotational constant, 183.3340 GHz, is close to that for *cis*-HDCCH (181.3 GHz) rather than that for *trans*-HDCCH (165.8 GHz) given by a CCSD(T)/aVTZ level calculation. The γ angle, between the principal axes of the observed magnetic dipolar interaction and the molecule-fixed axes, was calculated to be $29.3(26)^\circ$ confirming the observed HDCCH radical is the *cis*-HDCCH ($\gamma=28.9^\circ$) but not the *trans*-($\gamma=37.6^\circ$) form. Observed Fermi contact interaction constants for the b -proton ($a_F=176.45\text{ MHz}$) and b -deuteron ($a_F=16.66\text{ MHz}$) are also consistent with the estimated values (184.7 and 17.0 MHz) for *cis*-HDCCH from the hyperfine constants obtained by the ESR study in the Ar matrix [3]. The rotational spectra of the *trans*-HDCCH, however, have not been observed in supersonic jet. The zero point energy gap Δ_{tco} between the *trans*- and *cis*-tautomers estimated to be 33 cm^{-1} by the *ab initio* calculation is large enough only the *cis*-HDCCH tautomer is populated in the supersonic jet condition ($T \approx 15\text{ K}$).

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Accurate rotational fingerprints of radioactive radicals by mass-independent studies on AlO, TiO, and FeO

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Astrophysical observation of radioactive isotopes, like ^{26}Al , ^{44}Ti , or ^{60}Fe , provide insight into the nucleosynthesis processes of stellar cores[1]. The detection of characteristic photons which are released during radioactive decay is used to map their spatial distribution on large scale[2]. In general, the assignment to certain stellar objects fails due to limited sensitivity, exceptions are the nearby supernovae remnants *Cas A*[3] and *SN1987A*[4] for which the radioactive nucleus ^{44}Ti was detected.

An alternative approach to detect radioactive isotopes is to observe abundant molecules containing radioactive isotopes. This enables spectroscopic observation of rotational transitions by radio-telescope facilities, like *ALMA*. In the environment of stellar objects, the molecular condensation starts with simple diatomic particles containing oxides of refractory elements.

The astrophysical detection of diatomic radioactive molecules requires highly accurate rotational transition frequencies, which can be obtained from laboratory measurements of stable isotopologues and by applying the Dunham approach[5] to obtain scaled frequencies of radioactive isotopologues.

In this work, systematic studies are presented for ^{26}AlO , ^{44}TiO , and ^{60}FeO , as most promising stellar tracers of nucleosynthesis, based on high-resolution measurements on the rotational transitions of their abundant stable isotopologues (^{27}Al , $^{46-50}\text{Ti}$, $^{54,56-58}\text{Fe}$). Experiments were performed when a solid target (Al, Ti, Fe) is evaporated by a pulsed laser into an oxygen-rich buffer gas to form simple metal oxides. Adiabatically planar expansion of the gas jet into a vacuum chamber cools the gas to a few tens of Kelvin and subsequently, Doppler-free rotational absorption spectra are recorded in the frequency range up to 400 GHz.

A global data analysis, which also includes results from the literature, reveals the molecular structure beyond the Born-Oppenheimer (BO) limit, resulting in experimentally derived BO correction coefficients of these metal oxides for the first time. Based on this analysis, the rotational transitions of the radioactive molecules are determined with high accuracy at the sub-MHz level, which enables their unambiguous identification in stellar environments.

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Accurate sub-millimeter rest-frequencies for HCCO and DCCO radicals

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B2.4.

The ketenyl radical, HCCO, has been one missing link in interstellar oxygen-bearing chemistry, since it has been detected in only two starless cores so far. Its measured abundance is three orders of magnitude higher than predicted, meaning that there is one powerful formation mechanism still unknown. Moreover, its deuterated counterpart, DCCO, has never been identified in the ISM. HCCO and DCCO still lack of precise spectroscopic investigation although they exhibit a significant astrophysical relevance.

The present work has expanded the study of the ground-state pure rotational spectra of HCCO and DCCO into the sub-millimeter region.

The spectra acquisition was done with a frequency-modulation absorption spectrometer between 170 and 750 GHz. The radicals were produced in a low-density plasma by applying a negative glow discharge. For each isotopologue we were able to detect and assign more than 100 rotational lines.

The new measured lines have substantially increased the previous data set allowing the precise determination of high order rotational and centrifugal distortion parameters. In our analysis we take into account the Renner-Teller interaction between the ground state and a low lying excited state, enabling the prediction and assignment of up to $K_a=4$ rotational transitions.

The new set of spectroscopic parameters provide highly accurate, millimeter rest-frequencies of HCCO and DCCO for future astronomical observations. These results are very promising for a DCCO detection toward a starless core.

Terahertz spectroscopy of isotopologues of amidogen radical

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Amidogen is an asymmetric-top free radical that belongs to the nitrogen-hydrides family and it plays an important role as intermediate in the synthesis of interstellar ammonia.

The main isotopologue NH_2 and its ^{15}N -substituted variant have already been detected in the space, while no astronomical observations of the deuterated species of amidogen have been reported to date. In the last year, we focused our research activity on the study of the rotational spectrum of several deuterated isotopologues of amidogen radical, namely NHD , ND_2 , ^{15}NHD , and $^{15}\text{ND}_2$.

For the two former species, the measurements of the ground state spectrum was extended to the THz region and the newly recorded transitions were analyzed together with the literature data.

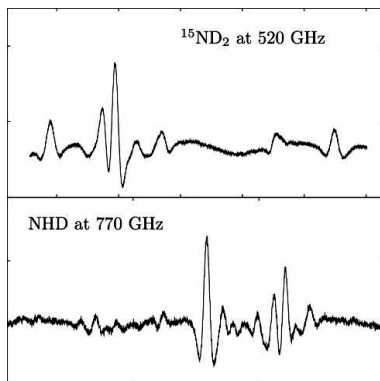
On the other hand, no laboratory detection for ^{15}NHD and $^{15}\text{ND}_2$ were reported so far and their pure rotational transitions have been observed for the first time from millimeter-wavelength to THz frequencies.

The recorded spectra show a fine-structure due to the electronic spin ($S = 1/2$) that couples with the rotational angular momentum ($J = N + S$) and a hyperfine-structure due to the nuclear spins I_{H} , $I_{^{15}\text{N}} = 1/2$, I_{D} , $I_{\text{N}} = 1$.

As example, a record of one fine-component of the $1_{11} - 0_{00}$ transition for two isotopologues is reported in Fig. 1.

The differences between the spectra have to be ascribed to two factors: (i) the magnetic hyperfine-constants whose value varies from isotope to isotope and (ii) the appropriate symmetry combinations of rotational and nuclear wavefunctions.

Indeed, since deuterium is a boson, the total molecular wavefunction must be symmetric upon the exchange of two identical nuclei only for the symmetric species ND_2 and $^{15}\text{ND}_2$.



Accurate rotational frequencies of deuterated Ammonium ions (d_1 – d_3) measured in a cryogenic ion trap

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B2.6.

Two of the most abundant nitrogen-bearing molecules in the interstellar medium are N_2 and NH_3 . Their protonated ions NH_2^+ (diazenylium) and NH_4^+ (ammonium) can provide critical information on interstellar chemistry. While N_2H^+ has been observed in many different sources, and it is, in fact, used as a proxy for N_2 , NH_4^+ being non-polar, cannot be observed through its rotational transitions. Nevertheless, it is predicted to be very abundant, since the proton affinity of NH_3 is very high, and it remains stable against collisions with the abundant H_2 . However, deuterated variants of NH_4^+ (d_1 – d_3) do possess small permanent dipole moments, and could be detected via rotational transitions. In fact, NH_3D^+ has been detected in space in Orion IRc2 and in the cold core B1–bS through its transition $J_K=1_0-0_0$ [1]. At the time of its detection, there were no laboratory data on the rotational spectroscopy of NH_3D^+ and the rest frequency was derived from an analysis of the high resolution IR spectrum of the ν_4 band [2]. The frequency was confirmed later by an accurate direct measurement in the mm-wave in a cryogenic ion trap in the Cologne laboratories [3]. In order to provide accurate rest frequencies for the other polar isotopologues, experiments have been performed in a cryogenically cooled ion trap using the state-dependent attachment of He atoms to ions as an action spectroscopy technique. Improved frequencies for NH_3D^+ as well as first direct measurements for $NH_2D_2^+$ and NHD_3^+ (guided by recent work by the group of D. Nesbitt [4]) have been obtained.

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The water vapor absorption continuum in the atmospheric windows at 4.0, 2.1, 1.6 and 1.25 μm

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While being implemented in most atmospheric radiative transfer codes, the amplitude, the temperature dependence and the physical origin of the water vapor absorption continuum constitute a long standing issue in molecular spectroscopy with direct impact in atmospheric and planetary sciences.

In this presentation we will review our recent measurements of the self- and foreign-water vapor continua at different spectral points of the atmospheric windows at 4.0, 2.1, 1.6 and 1.25 μm , by Cavity Ring Down Spectroscopy (CRDS) and Optical-Feedback-Cavity Enhanced Laser Spectroscopy (OF-CEAS) [1, 2]. The absorption continuum was derived either from the baseline variation of spectra recorded for a series of pressure values over a small spectral interval or from baseline monitoring at fixed laser frequency, during pressure ramps. After subtraction of the local water monomer lines contribution, self-continuum cross-sections, C_s , were determined with a few percent accuracy from the pressure squared dependence of the spectra base line level. The temperature dependence of the continuum of importance for atmospheric application was also obtained for some spectral points.

The measured cross sections constitute a unique set of accurate experimental constraints which have been used to adjust the last version (V3.2) of the semi-empirical MT_CKD water vapor continuum (Mlawer-Tobin-Clough- Kneizys-Davies) [3], widely incorporated in atmospheric radiative transfer codes (see Fig. 1).

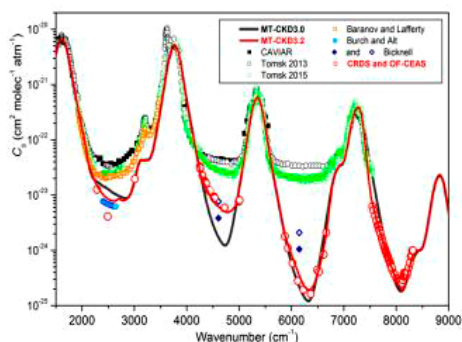


Figure 1. Comparison of the MT_CKD3.0 and 3.2 models (black and red solid lines, respectively) of the water vapor self-continuum cross-sections, C_s , in the 1500-9000 cm^{-1} range to an exhaustive collection of the experimental determinations available in the literature and obtained in this work (red circles).

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Sub-MHz deuterium spectroscopy and comparison with *ab initio* calculations of the line-shape effects

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In view of its simplicity, molecular hydrogen is the most appropriate chemically neutral system for testing quantum electrodynamics (QED) for molecules as well as for studies on new physics beyond the Standard Model [1] such as new forces. Theoretical predictions for energies of rovibrational transitions of hydrogen isotopologues are reaching $4 \cdot 10^{-5}$ cm⁻¹ accuracy [2–4]. In the Doppler limit line position of H₂, HD or D₂ becomes affected by the line-shape effects including its asymmetry [5]. Our experimental approach takes advantage of cavity-enhanced spectroscopy, and thereby we achieved sub-MHz level of accuracy on the weak quadrupole line position [4], typical for Doppler-free techniques.

To achieve kilohertz level of accuracy we applied *ab initio* quantum scattering calculations to describe the collisional line-shape effects. We performed measurements in several pressures to obtain determination of the line position free from systematic errors caused by incorrect line-shape characterisation. Similar *ab initio* line-shape model was tested in separate measurements with He perturber. Moreover, we extended our experiments to a wide range of temperatures and validated temperature dependences of line-shape effects. Line S(2) 2–0 of D₂ has been measured by the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) method assisted by an optical frequency comb (OFC) [6,7], using experimental setup described in Refs. [8,9].

The project is supported by the National Science Centre, Poland, Project Nos. 2015/19/D/ST2/02195 and 2015/17/B/ST2/02115. The research effort is part of the program of the National Laboratory FAMO in Toruń, Poland. The research effort is also supported by the COST Action CM1405 MOLIM.

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The high-resolution spectrum of DC₃N recorded in the infrared and millimeter-wave regions: a global analysis

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The observation of deuterated species in astronomical environments allows the determination of the H/D isotopic ratio, from which physical and chemical properties of astronomical objects can be deduced. DC₃N has been detected in several sources, most recently in the solar-type protostar IRAS 16293–2422 [1]. The laboratory work carried out so far is however still partial, since it concerns mainly pure rotational transitions [2,3] and, to a less extent, low-resolution infrared spectra [4]. The present work aims at providing a broad set of laboratory data in the infrared, millimeter- and submillimeter-wave regions. The infrared spectrum of DC₃N has been recorded at high-resolution (0.004 and 0.008 cm⁻¹) between 450 and 1600 cm⁻¹, where the fundamental bands ν_4 , ν_5 , ν_6 and their hot and combination bands are located. Moreover, the rotational transitions in the ground vibrational state and in the excited states $\nu_4=1, 2$, $\nu_5=1, 2$, $\nu_6=1, 2$, $\nu_7=1, 2, 3, 4$, $\nu_4=\nu_7=1$, $\nu_5=\nu_7=1$, $\nu_6=\nu_7=1$ have been recorded between 240 and 300 GHz, with the goal to extend the measurements to 1 THz. A global analysis which, besides the usual ro-vibrational Hamiltonian terms, accounts also for the predicted anharmonic resonances, is in progress. Eventually, a list of rest frequencies will be produced, in order to assist astronomical searches.

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Molecular hydrogen is the quantum molecular system to benchmark to challenge the fundamental physics, i.e., the Quantum Electrodynamics (QED), and the molecular Hamiltonians. Actually, soon or later, the accurate determination of the vibrational sequences of the molecular hydrogen isotopologues will open new perspectives for challenging the proton-to-electron mass ratio, and the proton radius size in a spectroscopy laboratory.

We will report on the first sub-Doppler determination of weak dipole transitions (forbidden in the Born-Oppenheimer approximation) in the $v : 2 \leftarrow 0$ overtone band of HD at $\lambda \sim 1.38 \mu\text{m}$. To saturate rovibrational transitions, we have implemented the Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) technique locked against a Cs-clock referenced Optical Frequency Comb (OFC).

The experimental sensitivity ($\sim 10^{-12}/\text{cm}^{-1}/\text{Hz}^{1/2}$) allowed us to determine the frequency center of 3 transitions (R_1 , R_2 and R_3) with an accuracy of the order of 20 kHz, i.e., with a gain of 3 orders of magnitude compared with the previous determinations. Under low pressure conditions, the broadening and frequency shift coefficients have been determined.

However, the shape of the observed NICE-OHMS resonances suffer from unexpected abnormal asymmetry which may be attributed to the hyperfine structure of the rotational levels. Nevertheless, the shape of the NICE-OHMS dispersion resonances, as well as their lack of amplitude suggests possible interfering crossover resonances. Furthermore, our frequency determination[1] of the transition does not match the value recently proposed by S.-M. Hu's group obtained by saturated CRDS (Lamb-dip)[2], as well as it barely matches the value proposed the Naples group (Doppler-broadened CRDS). These different transition frequency determinations, and the unexplained resonance shape can open the door to possible controversy that we will try to surround.

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IR laser spectroscopy of the deuterated isotopologues of ammonia

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Laser spectroscopy is performed in the near infrared to study the deuterated isotopologues of ammonia. Previous studies predicted a band in the range 6500–6800 cm^{-1} [1]. First experiments show the evidence of transformation of the gas ND_3 introduced in the cell which yields to the formation of ND_2H and NH_2D . At a first glance, no ND_3 transitions are present in this range of energy. First analysis will be presented with the isolation of the spectrum of each species.

C2.5.

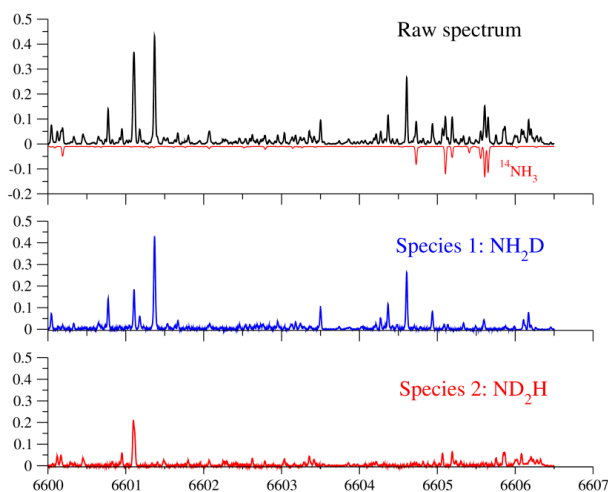


Fig. 1: Spectrum around 1514 nm. Impurity of $^{14}\text{NH}_3$ is present, the two spectra of NH_2D , ND_2H species have been isolated.

Photoacoustic spectroscopy of the oxygen a-band in support of OCO-2

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C2.6.

A number of remote sensing satellite missions using spectroscopic methods to interrogate atmospheric composition require accurate spectroscopic models for valid retrievals. The oxygen A-band (762 nm) is utilized for determination of air mass, solar pathlength, and surface pressure in remote sensing applications due to the uniform concentration of molecular oxygen throughout the atmosphere and the spectral isolation of the band. NASA's OCO-2 satellite uses the A-band as a reference to determine the global atmospheric carbon dioxide concentrations with an accuracy of 0.25%, placing stringent demands on our knowledge of the A-band spectral parameters. Current limitations in the A-band spectroscopic models, primarily from the treatment of line mixing (LM) and collision induced absorption (CIA), remain a significant source of error in carbon dioxide column retrievals. LM is manifested as intensity exchange due to collisional population transfer between closely spaced energy levels while CIA appears as a broad, weak continuum absorption feature arising from transient dipoles induced by molecular collisions. Photoacoustic spectroscopy, a zero-background technique with a large dynamic range, is an ideal method to observe these effects which become increasingly prominent at elevated pressures. We have developed a high precision (SNR>10,000), broadband photoacoustic spectrometer for recording full A-band spectra at room temperature. Unsaturated line-shapes are captured over a wide pressure range (300–3000 torr) to observe intensity exchange due to LM while maintaining high sensitivity to weak baseline features of CIA without interferences from instrumental background effects. Results from multispectrum fits of this data with non-Voigt line shapes showing insufficiencies in current A-band models will be presented.

Spin-torsion dominated hyperfine splittings in the first excited torsional state ($v_t = 1$) of Methanol

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A3.1.

Doublet, triplet and quartet hyperfine splittings have been observed in the E-species component of the first excited torsional state ($v_t = 1$) of CH₃OH. Four series of lines dominate the available data: (i) a $K = 6 \leftarrow 7$, Q branch series of quartets, with $7 \leq J \leq 15$; (ii) a $K = 3 \leftarrow 2$, Q branch series, with $3 \leq J \leq 18$, which starts as quartets, changes to doublets at $J = 7$, and then finally to singlets at $J = 17$; (iii) a $K = -2 \leftarrow -3$, P branch series of doublets, with $8 \leq J \leq 12$; and (iv) a $K = 8 \leftarrow 7$, Q branch series, with $8 \leq J \leq 24$, which starts as triplets and becomes doublets at $J = 15$. There are also a few isolated doublets and quartets, which do not form long spectroscopic branches. We have modeled the hyperfine quartet and doublet splittings with empirically chosen symmetry-allowed spin-torsion and spin-rotation interaction terms appropriate for the two $I = \frac{1}{2}$ spin systems arising from the OH proton and from the CH₃ protons, respectively, and have achieved a least-squares fit of 144 hyperfine components (88 hyperfine intervals to six hyperfine parameters with a standard deviation (0.97 kHz) near experimental measurement accuracy. The physical effects included in the present Hamiltonian differ from those included in the Hamiltonian for our earlier work on hyperfine splittings in $v_t = 0$ E states, because the experimentally observed $v_t = 1$ splittings are found to decrease approximately as $1/J$, whereas the $v_t = 0$ splittings increase approximately as J . The position and relative intensities of the weak central features of the triplets can be explained as three-level Λ -type crossover resonances. Our fitted Cxx-OH, CyyOH and CzzOH empirical spin-rotational parameters compare well with ab initio calculations in the literature, and our fitted CzaOH and CzaCH₃ empirical spin-torsion parameters agree and disagree with ab initio calculations in the literature.

Extension of the normal mode approach to nonrigid polyatomic molecules

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A3.2

In this talk, we will present an extension of our theoretical approach initially designed for semirigid molecules to more complex systems having at least one large amplitude motions (LAM) commonly known as nonrigid (floppy) molecules. This study will be essentially based on the Hamiltonian introduced in 1970 by Hougen, Bunker and Johns [1], the so-called HBJ model which could be considered as the nonrigid extension of the Watson–Eckart Hamiltonian. A complete and detailed derivation based on the HBJ approach with application to triatomic floppy molecules was made by Jensen [2]. A formulation in terms of internal coordinates has been carried out in [3]. One of the specificities of the present work is the possibility of using most of the tools previously developed in our laboratory for semirigid molecules (reduced Hamiltonian, compressed basis sets, tensor operators, etc.), with only some minor changes. Here, we have chosen a formulation quite different from what is usually done in the literature. To this end, the numerical treatment of the LAM coordinate is replaced by an algebraic formulation where all matrix elements (both for the small and large amplitude vibrations) are computed analytically to make variational calculations faster [4]. Illustrative examples will be given.

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Essentially free internal rotation of the Propynyl Methyl group investigated by microwave spectroscopy

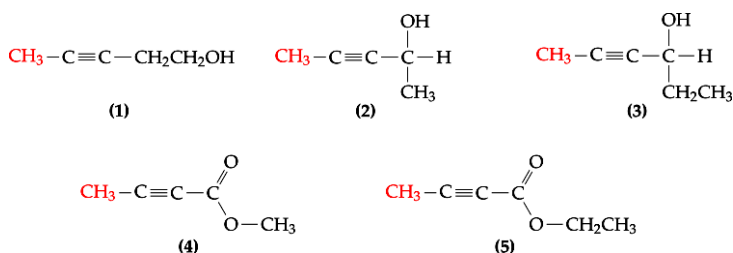
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Fourier transform microwave spectroscopy has become the most important method to investigate large amplitude motions of a molecule, where internal rotation is among the main fields of interest. Due to higher resolution and more accurately determined molecular parameters in comparison to for example fluorescence or electronic spectroscopy, many barriers to internal rotations have been determined by this method. Still only very few molecules with barriers lower than 30 cm⁻¹ have been studied. The rotational spectra of such molecules are hard to assign and model because of large torsional splittings up to several GHz and because high order terms in the Hamiltonian are often required to reproduce the spectra to experimental accuracy. A very low barrier to internal rotation arises by separating the methyl rotor from the rest of the molecule by the acetylenic group with cylindrical symmetry. Only six molecules of the type CH₃-C≡C-R had been studied by microwave spectroscopy before (R = CD₃, SiH₃, CH₂OH, COF, COOH, CH₂Cl [1–6]). The three-fold barrier to internal rotation of the CH₃-C≡C- methyl group (the propynyl methyl group) is lower than 10 cm⁻¹ in all cases.

This work presents the microwave studies and quantum chemical calculations carried out at the MP2/6-311++G(d,p) level of theory on 3-pentyn-1-ol (**1**, R = CH₂CH₂OH, $V_3 = 9.4552(94)$ cm⁻¹ [7]), 3-pentyn-2-ol (**2**, R = CH(OH)-CH₃, $V_3 \approx 9.0$ cm⁻¹), 4-hexyn-3-ol (**3**, R = CH(OH)-CH₂CH₃, 3 conformers, $V_3 = 7.161012(7)$ cm⁻¹, 4.2365(26) cm⁻¹ and 7.9016(39) cm⁻¹), methyl-2-butynoate (**4**, R = COOCH₃, $V_3 = 0.4690(36)$ cm⁻¹) and ethyl-2-butynoate (**5**, R = COOCH₂CH₃, 2 conformers, $V_3 = 0$ cm⁻¹ and 0 cm⁻¹). The experimental spectra were reproduced to measurement accuracy using the programs XIAM and BELGI. The determined barriers to internal rotation are very low as expected, and seem to decrease with increasing length of the carbon chain.



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Microwave spectroscopic and quantum chemical studies of the coupled large amplitude motions in S-Phenyl Thioacetate

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S-Phenyl thioacetate belongs to the thio analogs of the class of unsaturated acetates, which were well-investigated using microwave spectroscopy e. g. butadienyl acetate [1], vinyl acetate [2], and isopropenyl acetate [3]. In contrary to the planar butadienyl and vinyl acetate, isopropenyl acetate has a non-planar structure. This leads to a significant difference in the barrier height to internal rotation of the acetyl methyl group ($151.492(34) \text{ cm}^{-1}$ for vinyl acetate and $135.3498(38) \text{ cm}^{-1}$ for isopropenyl acetate). S-phenyl thioacetate is a challenging project, especially regarding the questions of planarity and barrier height.

Quantum chemical calculations were performed with the B3LYP and MP2 methods in combination with different basis sets. All levels of theory yielded a pair of enantiomers as the most stable structure of S-phenyl thioacetate. The acetyl methyl group undergoes internal rotation with a predicted barrier height in the range of $48\text{--}72 \text{ cm}^{-1}$, depending on the applied method. A further large amplitude motion, the tunneling of the phenyl group, also occurs. Accordingly, the potential energy curves for the phenyl torsion features double minima and the $v_t = 0$ state is lower in energy than the local maxima. Though the $v_t = 1$ state transitions are too weak to be detected under our measurement conditions, Coriolis interaction still leads to significant shifts of the $v_t = 0$ state lines if compared to the predicted frequencies. This tunneling motion of the phenyl ring coupled with the methyl internal rotation with relatively low barrier height complicated the assignment tremendously. Nevertheless, the microwave spectrum was assigned successfully. However, developing an appropriate Hamiltonian to correctly capture the large amplitude motions of S-phenyl thioacetate is indispensable and currently in progress.

Finally, a comparison is drawn to the oxygen-analogon phenyl acetate, phenyl formate [4], as well as the *anti,anti*- and *anti,gauche* conformers of ethyl thioacetate [5].

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Separately fitting the torsional symmetry species of molecules with one or multiple internal rotor(s)

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In the last decade molecular jet based Fourier transform microwave (MJ-FTMW) spectrometers have become more and more popular. The complexity of molecules studied by the MJ-FTMW method also increased dramatically. Molecules with one or two internal rotor(s) and low potential barriers are quite commonly investigated systems today, and also studies on three- or four-rotor molecules exist.

In many cases all torsional symmetry species can be observed in the ground state ($v_t = 0$) but not in the excited states. Therefore, it is usually not possible to discriminate between V_3 and V_6 contributions to the potential function. It is also difficult to fit potential coefficients and the moment(s) of inertia of the internal rotor(s) simultaneously, and the determination of potential coupling terms often fails.

For all these reasons it is useful to fit the different symmetry species separately. This is a well-known method for the A species where a rigid rotor Hamiltonian supplemented by centrifugal distortion terms can be applied. It is also possible to do this with any other symmetry species if angular momentum operators of odd power, e.g. P_z , P_x , P^2P_z , are included in the Hamiltonian. We wrote a computer code, which allows to define any possible operator composed of linear combinations of products of P_z , $P_x = P_x + iP_y$, and $P_- = P_x - iP_y$ directly in the input file. In addition, nuclear quadrupole coupling of one nucleus can be treated in a first order approach.

We will present details of the new computer code and give some applications for molecules with one to four internal rotors with and without nuclear quadrupole coupling, as well as discuss how the odd-power parameters can be interpreted in terms of torsional barriers, and how they can be used to identify an observed symmetry species. Because the new code is rather fast, some sample fits will be run during the presentation.

High resolution Rydberg spectroscopy of 3d metal sandwich compounds: ultrasensitive probing the electron density changes in organometallic molecules

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This year chemists celebrate a centenary of transition-metal sandwich compounds representing one of the most intriguing classes of organometallics. A unique spectroscopic property of these systems consists in a presence of clearly-defined Rydberg transitions in their gas-phase absorption and ionization spectra. No other organometallic molecules reveal such features. The lower-lying Rydberg excitations in sandwiches originate at a non-bonding metal d_{z^2} orbital and their structures provide invaluable information on the ionization energies, molecular symmetries and configuration interactions. Reliable assignments of Rydberg transitions made on the basis of the corresponding term values play key roles in verification of time-dependent DFT calculations of sandwich electronic excited states [1]. The low-lying Rydberg states of sandwich molecules can work as intermediate levels in multi-photon laser ionization processes.

The resonance enhanced multi-photon ionization (REMPI) spectra provide precise electronic energies and vibrational frequencies of excited sandwich systems. The high-resolution REMPI spectra of a prototypic sandwich molecule, bis(benzene)chromium, and its deuterated analogue in the $d_{z^2} \rightarrow 4p_{x,y}$ region reveal rich vibronic structures which are indicative of Jahn-Teller (JT) instability. The TD DFT optimization of the Rydberg-state molecule demonstrates that the JT geometry distortion is closely related to the electron density changes on the excitation. In contrast to another well-known JT system, the $C_6H_6^+$ ground-state cation, where the largest JT contributions are provided by the vibrations involving the carbocycle, the main JT active modes in the Rydberg-state $(C_6H_6)_2Cr$ correspond to the CH bend. This difference can be easily correlated with the nature of the degenerate molecular orbitals responsible for the JT effect.

On the other hand, the sandwich carbocycle JT distortion is revealed by the mass-analyzed threshold (MATI) spectrum of cobaltocene. The MATI peaks arise from the Rydberg levels characterizing by principle quantum numbers $n > 100$. The high-resolution vibronic structure of this spectrum shows the components corresponding to the out-of-plane carbocycle deformation which agrees very well with the electron density change on ionization. This change involves also the metal electrons. Accordingly, the cobaltocene MATI spectrum reveals a contribution from the skeletal e_1 mode active in the second-order JT effect. These examples demonstrate that high-resolution Rydberg spectroscopy provides an extremely sensitive instrument for studying electron density changes in sandwich molecules. Recent results on other sandwich systems will be given in the presentation.

Acknowledgements

This work was supported by the Russian Science Foundation (Project No. 18-13-00356).

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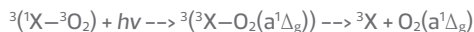
Two-color REMPI [(1+1')+1] of the singlet oxygen $^1\text{O}_2$ arising in UV-photodissociation of van der Waals complex $\text{C}_5\text{H}_8\text{-O}_2$

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Photochemistry of the molecular oxygen is important for manifold of atmospheric and photobiological processes. Van der Waals complex of oxygen X-O_2 has been shown to be a good model for the study of UV photophysics and photochemistry of the oxygen perturbed by environment [1]. The new supramolecular photoprocesses in X-O_2 complexes have been revealed. One of them gives rise to the singlet oxygen $\text{O}_2(a^1\Delta_g)$ which is interpreted to be due to supramolecular transition in complex with simultaneous change of the spin of complex partners (double spin-flip) [2]:



The singlet oxygen formation was detected with its photodissociation by the same laser pulse with formation of two atoms with specified kinetic energy measured by velocity map imaging technique (VMI). Spectral range of one-laser experiments is limited by wavelength of REMPI of oxygen atoms near 225 nm. Another way to detect the singlet oxygen is REMPI (2+1) itself in spectral range 300–340 nm [3].

In present work the one-laser approach for detection of the singlet oxygen is applied with two color REMPI [(1+1')+1] of singlet oxygen where dye laser radiation (455 – 469 nm) and its second harmonic are used simultaneously. In this approach the same excited intermediate states of O_2 have been used. UV-radiation wavelength is within the spectral region of 227–235 nm where photodissociation of the Van der Waals complex of isoprene with oxygen $\text{C}_5\text{H}_8\text{-O}_2$ is known to give rise to singlet oxygen [2]. This approach in combination with VMI has been applied to detect the singlet oxygen arising from van der Waals complex $\text{C}_5\text{H}_8\text{-O}_2$.

This work has been supported by Russian Science Foundation (grant 16–13–10024).

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The vibrational structure of the $\text{NO}_3 \tilde{X}^2\text{A}_2'$ state studied by SVL DF spectrum

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We have generated NO_3 in a supersonic free jet expansion, and observed laser induced fluorescence (LIF). We have measured the LIF excitation spectrum and dispersed fluorescence (DF) spectra from single vibronic levels (SVL). Vibrational structure of the DF spectrum from the vibration-less level is categorized into three parts. Region I: The ν_1 and ν_3 regions, ~ 1050 and 1500 cm^{-1} , respectively, are now under active discussion, and will be discussed elsewhere. Region II: The structure in the region below 1850 cm^{-1} , excluding Region I, is relatively simple, and is the topic of the present paper. Region III: The structure above 1850 cm^{-1} is too complicated to interpret. The vibrational analysis of Region II is straightforward; the vibrational structure consists the ν_4 progression and its combination with ν_1 , 4^0_n and $1^0_1 4^0_n$, $n = 0, 1$, and 2 , respectively, where ν_1 and ν_4 are totally symmetric stretching and asymmetric bending vibrational modes, respectively. One of the most remarkable features of the structure is the intensity pattern of the two progressions; although ν_4 is an e' mode, they display a 'regular' intensity distribution, where 'regular' means intensity gradually decreasing with increasing the ν_4 vibrational quantum number, n , above. The 'regular' structure is unusual as a progression of a degenerate mode, which usually shows an 'alternate' intensity distribution, where significant intensity is limited to even quantum numbers, $n = 0, 2, 4, \dots$. Some of the unusual structures of other systems have been successfully interpreted, e.g. a discussion by Herzberg, but the previous interpretations cannot be applied to the present NO_3 system. To explain the unusual intensity distribution of the ν_4 progressions, we propose the following original interpretation; on the vibrationally excited ν_4 levels, the electronic and vibrational wave-functions are strongly coupled, and behave as vibronic wave-functions, $|K; \Lambda; \nu_4, l\rangle \neq |\Lambda\rangle|\nu_4, l\rangle$.

Line shape study of oxygen B-band with CRDS in Dual-Beam configuration

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Oxygen B-band, despite its low intensity, has recently been recognized as a valuable tool in atmospheric studies. If used together with about 15 times stronger A-band, it leads to increased measurement accuracy in several applications such as determination of pressure and temperature profiles in the atmosphere, remote clouds observations and stratospheric winds detection.

The B-band is characterized by very low line intensities (below 6·10⁻²⁵ cm²/molecule), which causes that the accurate laboratory measurements require techniques supported by an optical cavity. We present results of our recent investigations of O₂ B-band line shapes performed with one of the most sensitive absorption-based measurement techniques, which is cavity ring-down spectroscopy (CRDS).

We used an optical frequency comb (OFC) assisted, Pound-Drever-Hall (PDH) locked, frequency stabilized cavity ring-down spectrometer (FS-CRDS) [1]. In a present setup the probe laser beam was split into two beams of orthogonal polarizations: locking beam and actual probe beam, detuned from each other by one cavity free spectral range (FSR), similarly as in Ref. [2]. With this system we investigated the influence of the probe beam detuning from the cavity resonance, as well as its incomplete switching and phase shift of incident light during amplitude switching, on the observed pumping and decay signals. We show that this can significantly affect ring-down signals and leads to systematic errors in measured absorption coefficient. All of this can be simulated with the use of a simple analytical model [3].

The change from single to dual-beam configuration of the CRDS together with accurate switching of the probe beam enabled a significant increase of a signal-to-noise ratio (SNR) in measured spectra. The quality of spectra, measured by quality of the fit parameter (QF) can be as high as 40000 in a single scan. This sensitivity is high enough to record the quadrupole transition T5 S6 with intensity of about 1.4·10⁻³⁰ cm²/molecule.

Transitions from the O₂ B-band located near 690 nm were studied. Detailed analysis of P9 P9 line shape shows that its accurate modelling even in the pressure range as low as 10 Torr (1.3 kPa) requires accounting for the effects of speed-dependence and the Dicke narrowing [4] simultaneously. For the P1 P1 line, measured in the pressure range up to 24 Torr (3.2 kPa), this is even more clear.

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LIF Spectrum of a $^1\Sigma$ species containing Si: linear SiOSi ?

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In our past SiCN investigation [1], we found unknown bands with $^1\Pi - ^1\Sigma$ rotational structure in the laser induced fluorescence (LIF) excitation spectrum of SiCN. Dispersed fluorescence (DF) spectra from single vibronic levels have fairly long progressions with very harmonic structure, but no hot-band structure. From the rotational constants, the spectral species may possibly be attributed to SiOSi. The most stable geometry of the ground electronic state is reported to be cyclic by CCSD(T)/cc-pVTZ level calculation [2]. Our CCSD(T) calculation with arg-cc-pCVTZ indicates a linear geometry, $^1\Sigma_g^-$, lying $\sim 2,000\text{ cm}^{-1}$ above this lowest cyclic structure. More advanced calculations by CAS-SCF and MR-CI indicate that the most stable cyclic geometry correlates to $^1\Delta_g$, which is the ground electronic state, and the $^1\Sigma_g^-$ state is the lowest excited state, lying $\sim 800\text{ cm}^{-1}$ above the $^1\Delta_g$ state. For the ground electronic state consisting of the cyclic and $^1\Delta_g$ linear geometries as the two minima, our calculation predicts a strange potential energy surface: the state has a $\sim 1,000\text{ cm}^{-1}$ barrier from the cyclic structure to the linear geometry. In contrast, the $^1\Sigma_g^-$ state is predicted to have a linear structure as a single minimum. At present, we postulate that our unknown spectrum may be attributed an electronic transition from the low-lying $^1\Sigma_g^-$ state to a $^1\Pi$ electronic state. More precise computational studies are currently underway.

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Local interactions of the asparagine and histidine aminoacids in a protein chain: gas phase conformer-selective IR spectroscopy of model molecules

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Polar residues of proteins, having both donor and acceptor sites, are known by biochemists as promoters of secondary structures such as gamma- and beta-turns. The possibility to locally anchor their side chain (SC) to the main chain (MC) through H-bonding involving side chain polar sites is expected to be at the heart of this behavior.

We will document this H-bond-based anchoring through a gas phase approach that consists i) first, in determining the UV spectroscopic features of the conformations adopted by model peptides (Scheme 1) having a polar neutral residue, such as asparagine (Asn^[1]) and histidine (His^[2]), and ii) second, in determining the intramolecular H-bonds interactions that stabilize them, using a double resonance IR/UV laser spectroscopic approach based on laser-desorbed jet-cooled molecules coupled to quantum chemistry calculations.^[1,2] It will be shown that the local anchoring of the Asn and His side chains (respectively bearing a carboxamide and an imidazole ring) consists of SC-MC and MC-SC H-bonds, which are consistent with the γ - and β -turn backbone secondary structures observed in proteins and contribute to stabilize them.

These gas phase structural data, relevant to a hydrophobic environment, have been used as a reference^[1,2] to assess the anchoring taking place in high resolution crystallized proteins of the Protein Data Bank.^[3] This approach reveals that the stronger MC-SC bonds are preserved in many cases whereas the SC-MC bonds are always disrupted, in qualitative agreement with the gas phase ranking of their strength.

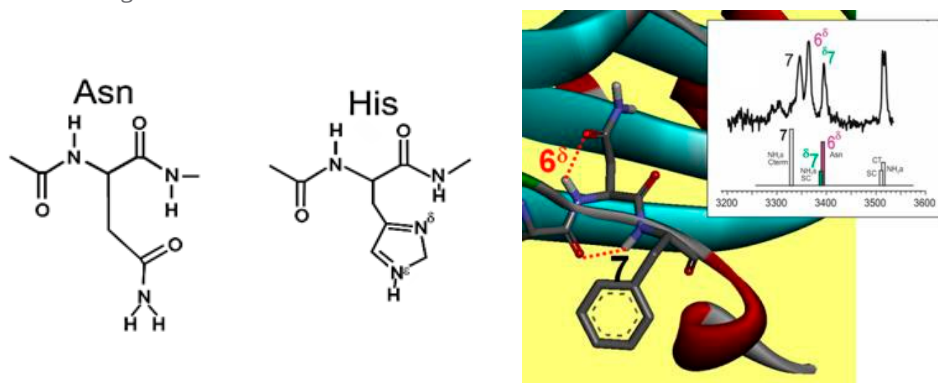


Figure: Example of a conformer-selective IR spectrum (insert) of a model peptide containing an asparagine residue ($-\text{CH}_2-\text{CONH}_2$ side chain) in the NH stretch region, recorded by IR/UV double resonance spectroscopy, illustrating the presence of local main chain/side chain H-bonds, together with an example of the same H-bonding pattern (coloured picture) as found in a protein of the Protein Data Bank.^[3]

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Water Sculpts the Distinctive Shapes and Dynamics of the Tn Antigens: Implications for their Molecular Recognition

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The Tn antigen is one of the most widely studied antigens related to cancer. It includes two variants, GalNAc-*O*-Thr and GalNAc-*O*-Ser which differ only in a methyl group. However, despite their structural simplicity and similarity, they display different conformations in solution, which can have significant biological repercussions.[1]

The NMR data and molecular dynamics (MD) simulations show that in GalNAc-*O*-Thr derivative the carbohydrate moiety is almost perpendicular to the peptide backbone and in the glycosylated Ser variant, the sugar adopts a parallel disposition.[2] This characteristic 3D orientation of the carbohydrate in both compounds leads to different first hydration shells and postulates the existence of water molecules in both antigens that bridge the carbohydrate and the peptide moieties.

A multidisciplinary approach that includes the synthesis, experimental and theoretical study of the Tn antigens in the gas, solution and solid phases has been applied to deduce the key role of water in the modulation of the conformational preferences of these molecules and therefore in their presentations for interacting with protein receptors. Both modified Tn antigens were evaluated in the gas phase, using mass- and conformer-selected infrared laser spectroscopy and coupled with quantum chemical computations.[3] The results obtained were supported by crystal structures of two designed glycopeptides bound to an antibody. [4]

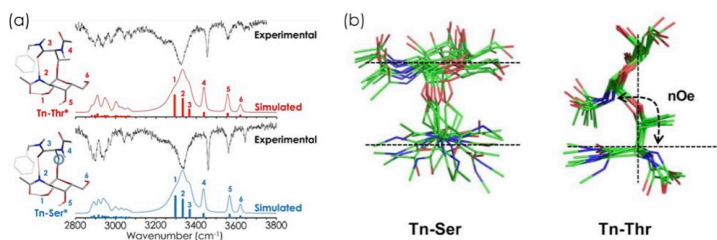


Figure 1. (a) IRID spectra of Tn-Thr* and Tn-Ser* Antigens. (b) Conformation in solution of Tn-Thr and Tn-Ser.

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Testing the parity symmetry in cold chiral molecules using vibrational spectroscopy

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Parity violation (PV) has never been observed in chiral molecules. Caused by the weak nuclear force, PV should lead to a tiny energy difference between the enantiomers of a chiral molecule, and in turn to frequency differences in the rovibrational spectra of the two enantiomers of a chiral molecule. A successful PV measurement will shed some light on the origins of biomolecular homochirality. It can also constitute a test of the standard model in the low-energy regime and a probe of physics beyond it, and serve as a stringent benchmark in relativistic quantum chemistry calculations. We present our ongoing work towards developing the technologies needed for measuring PV in chiral molecules via Ramsey interferometry in the mid-infrared. This includes amongst other things developing frequency stabilised quantum cascade lasers calibrated against primary standards and a buffer-gas source of organo-metallic species of interest for a PV measurement formed using laser ablation of solid-state molecules in a cryogenic cell containing gaseous helium at 4 K. We also present the results of preliminary spectroscopic investigations conducted on various species, in particular methyltrioxorhenium (MTO), an achiral test molecule from which promising chiral derivatives have recently been synthesized. We report on the high-resolution spectroscopy of MTO, both in cells and in molecular beams, at various temperatures and resolutions.

Hydrated Lewis antigens in the gas phase: building up the environment or peeling off the solvent?

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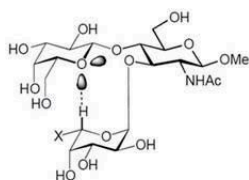
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Sialyl LewisX and the structurally related trisaccharide Lewis X antigen (LeX) are important carbohydrate as they are recognized by several selectins involved in fundamental pathogenic biological processes. As a consequence, they have been the target of many studies trying to design drugs mimicking them. Most molecular recognition processes are initially driven by "shape recognition" between the receptor and the ligand. A good understanding of the conformational preferences of a molecule is then a requisite starting point for the design of mimetic drugs. In that view, there has been tremendous efforts in resolving the structural properties (conformation, flexibility, specificity) of LeX bound to selectins or in a solvent. These have shown that the bioactive conformation of LeX adopts a stacked arrangement of its Fucose and Galactose components, stabilized by an unconventional CH \rightarrow O "hydrogen bonding".[1] In contrast, previous gas phase studies showed that the intrinsic preferred conformation of Lewis X, free of any perturbation from the environment, was stabilized by cooperative OH \rightarrow O interactions where the Fucose and Galactose units are hydrogen bonded instead of stacked.[2] This suggested an important role of the solvent in the bio-activity of LeX. In this study, we have then studied the conformational preferences of the hydrated clusters of LeX by a combination double resonance IR-UV laser spectroscopy experiments and computational quantum chemistry conformational landscape exploration. Thanks to the stabilization of large hydrated clusters of LeX we could observe, in the gas phase, its solvent phase, bioactive conformation.

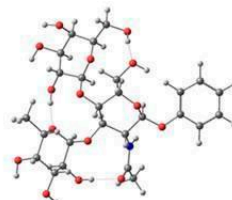
Our results show how important structural water molecules are in the shaping and fine-tuning of carbohydrate bio-active conformations. Their effect must be well taken into account to better scrutinize their functioning and progress towards a rationalization of the design of new drug-like mimetics.



Bioactive Lewis X



Stacking conformation
Of Lewis X - H₂O



Cooperative conformation
of isolated Lewis X

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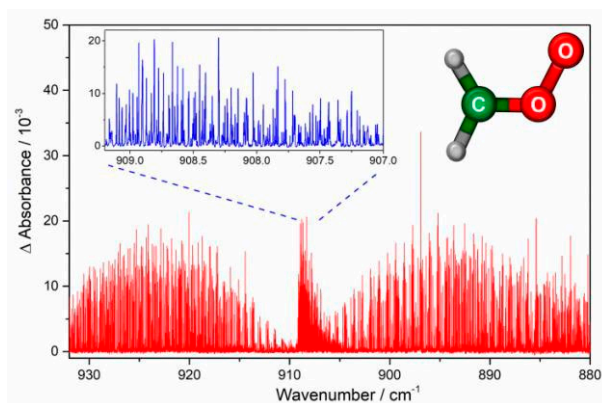
High-resolution ro-vibrational spectrum of the simplest Criegee intermediate CH_2OO between 880 and 932 cm^{-1}

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The Criegee intermediates, carbonyl oxides produced in the ozonolysis of unsaturated hydrocarbons, play important roles in atmospheric chemistry. CH_2OO is the simplest Criegee intermediate and its characterization is important for investigations of its reaction mechanisms and molecular structure¹⁻⁵. In this work, we report the high-resolution ro-vibrational absorption spectrum of CH_2OO recorded with a tunable cw external-cavity quantum cascade laser (EC-QCL) coupled with a Herriott multi-pass absorption cell; the system covers a wide spectral range (880–932 cm^{-1}) with optical resolution 0.0015 cm^{-1} . Over one thousand lines are assigned to determine the spectral constants of the OO-stretching (ν_6) mode of CH_2OO . Perturbations in some rotational levels of this mode are also identified and analyzed. Furthermore, a group of lines near 899.5 cm^{-1} are identified to be associated with the hot band because their temporal profiles are distinct from those of the ν_6 band.



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Investigation of the ν_8 and ν_{21} bands of propane $\text{CH}_3\text{CH}_2\text{CH}_3$ at 11.5 and 10.9 μm : evidence of large amplitude tunnelling effects.

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We present detailed investigations of the ν_8 band (C-C symmetric stretch at 870 cm^{-1}), an ν_{21} band (CH_3 rock at 921 cm^{-1}) of propane (C_3H_8). For both bands the rotational energy levels in the upper states are split because of interactions with the internal rotations of the methyl groups, leading to the identification of AA, EE, AE and EA torsional components. One of the results of the present study is to show that these torsional splittings are due to the existence of anharmonic and Coriolis resonances, coupling the 2^1_1 and 8^1_1 rotational levels to nearby highly excited levels of the two internal rotations of the methyl groups. An effective "vibration – torsion – rotation" Hamiltonian model was built in the G_{36} symmetry group which accounts for both types of resonances. In parallel, a code computing the line intensities was developed to allow unambiguous torsional component assignments. The line assignments were performed using a high resolution (0.0015 cm^{-1}) infrared spectrum of propane, recorded with synchrotron radiation at the SOLEIL French light source facility coupled to a Bruker IFS-125 Fourier transform spectrometer.

High resolution FTIR study of the ν_6 band of CH_2F_2 in 3 μm spectral region at low temperatures

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Difluoromethane belongs to the class of Freons, which are potential replacements for the ozone depleting 'chlorofluoro carbons' as refrigerants. Owing to its dense energy levels, it also serves as an ideal system for basic understandings on vibrational energy re-distributions. In this context, 3 μm region is particularly interesting as it contains fundamental (ν_1 and ν_6), combination ($\nu_2+\nu_8$) and overtone ($2\nu_2$ and $2\nu_8$) vibrations. The earlier studies carried out in this region [1–3] have highlighted the possibilities of couplings between various energy levels, which necessitates comprehensive studies of the rotationally resolved vibrational modes. Cooling of the gas sample is one of the effective methods in such cases, which can be used to decongest the spectrum and reduce the Doppler width. Consequently, a jet-cooled study of the ν_6 band (C–H asymmetric stretch, C–type band with origin at $\sim 3014.05046\text{ cm}^{-1}$) had been carried out [4]. However, because of the introduction of extra cooling, the higher states were not populated and thus a total of only 286 transitions up to $J \leq 19$ and $K_a \leq 4$ could be assigned.

Hence, the present work is aimed at studying the transitions of ν_6 band involving high J and K values along with reduced Doppler width of spectral lines so as to obtain precise molecular constants. We have adopted a static cooling approach with a temperature of $\sim 160\text{ K}$ estimated at the sample, which has drastically improved the spectral profile as compared to the room temperature spectrum, as shown in Figure 1 describing the ' Q_6 ' transitions. The spectra were recorded using an indigenous 26 cm long metallic cell using Bruker-IFS 125HR FTS instrument at an unapodized resolution of 0.0025 cm^{-1} . Precise value for the band origin and centrifugal distortion constants up to 3rd order have been obtained by fitting ro-vibrational transitions upto $J \leq 50$ and $K_a \leq 14$ using Watson's A-reduced Hamiltonian in the I' representation. The details of various vibrational levels lying in this region and the possible coriolis interactions between them will be presented.

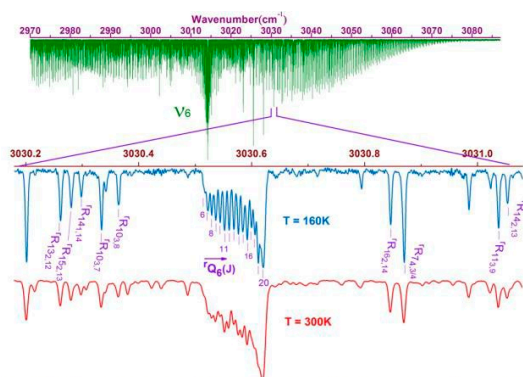


Figure 1: High resolution spectrum of ν_6 band of CH_2F_2 . The (lower) expanded view of ' Q_6 ' transitions at room temperature and 160K.

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The NH₂ scissors band of Methylamine

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A4.3

Methylamine is a prototypical molecule with two large amplitude degrees of freedom: CH₃ internal rotation and NH₂ inversion which are strongly coupled and give rise to a rotation-inversion-torsion structure in the vibrational states.

For the first time a rotationally resolved spectrum of methylamine was recorded in the spectral region of the n₄ NH₂ scissors vibration using two infrared spectroscopic methods: a White-type multipass cell device (150 m optical path) coupled to the Bruker IFS 125 HR Fourier transform spectrometer implemented on the AILES beamline at the SOLEIL synchrotron facility, enabled to record a room temperature spectrum of the whole band in the 1540–1710 cm⁻¹ range at the maximal resolution of 0.001 cm⁻¹, and a quantum cascade laser spectrometer tunable around 6.2 μm coupled to a pulsed supersonic jet [1] (2.5 % CH₃NH₂ seeded in 5 bar neon) was used to record a low temperature high resolution spectrum in the 1622–1655 cm⁻¹ range of the n₄ R branch.

The goal of this work was to assign and analyze the NH₂ scissors band. The unresolved band contour of the NH₂ deformation of methylamine was observed around 1623 cm⁻¹ [2]. It is a hybrid band of A' symmetry in the C_s group (B₁ symmetry in the G₁₂ of PI group) with components of dipole moment change both parallel and perpendicular to the C–N bond. Using the LWW program adjusted for methylamine [<http://www.lww.amu.edu.pl>], it was possible to identify about 1000 transitions of B, E₁₊₁, E₁₋₁, and several lines of E₂₊₁ and A symmetry. The analysis of the NH₂ deformation IR band was supported by the laser spectrum: the rovibrational cooling of the supersonic expansion simplifies the congested rovibrational structure observed at room temperature, which makes easier to interpret sharp and well isolated lines. All assignments were confirmed with the GSCD. The attempt of global fit was made using a group theoretical formalism [3].

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Wrong distance – wrong line strength – wrong concentrations

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In the 60s D. Herriott, H. Kogelnik, and R. Kompfner published the concept of the so-called Herriott-cell. Two facing spherical mirrors build an optical multipass cell for long optical pathways, which are often used to measure low gas concentrations or the according absorption line parameters. This cell is used in various applications and its importance might become obvious from the fact, that this publication was cited more than 800 times.

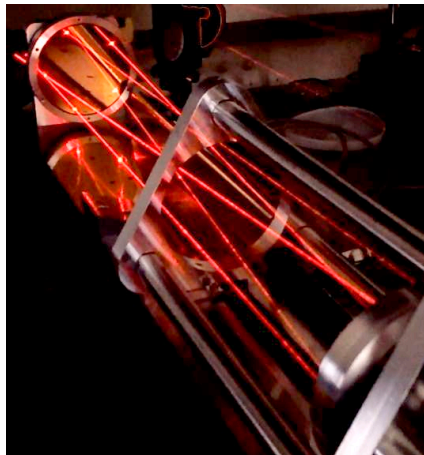
Although it has been quoted so often, no one has apparently noticed a mistake in the formula for the distance 'd' of the Herriott-cell mirrors that is needed to realize a so-called closed configuration.

The formula is: $\cos(\theta) = 1 - (d/2f)$

In fact, the mirrors need to be placed slightly further apart. How much further depends on the individual configuration and was derived in the work presented here.

Based on this wrong formula for the mirror distances, J. Altmann, R. Baumgart, and C. Weitkamp calculated the optical path length for the multipath cells of the Herriott-type and published it in the 80s. Consequently, these theoretical path lengths are also deviating from the real ones. These wrong formulas have been used for the measurement of thousands of line intensities which can be found in various data bases.

Especially for complex models, like climate models, small changes in the parameters are leading to tremendous changes in the results. Accordingly, sub-percent uncertainties are targeted for line strength parameters and thus for gas concentrations measured via absorption spectroscopy. To realize these, the correct formula for the optical path length must be considered, because the deviations are typically of the same order of magnitude.



On not yet solved problems concerning some molecular systems investigated by rotational spectroscopy along my research life

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Not yet solved aspects of the rotational spectra of some molecular systems will be discussed. They concern: 1) Unsatisfactory analyses of the spectra; 2) Non-observation of expected rotational transitions; 3) Non observation of the spectra of expected chemical species.

Rotational spectrum and molecular structure of succinic anhydride aided by computational calculations

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2) *Gottfried-Wilhelm-Leibnitz-Universität*

The cm-wave and mm-wave spectra of succinic anhydride have been studied in a pulsed supersonic jet using Fourier-transform microwave spectroscopy and in a free-jet using mm-wave absorption spectroscopy. All rotational constants, quartic centrifugal distortion constants are determined. Studies on ¹³C and ¹⁸O singly substituted isotopologues were used to assign the substitution geometry for succinic anhydride. The transitions observed in the FTMW spectrum show fine structure. The fine structure can be fitted by including spin rotation constants for the equivalent hydrogen nuclei but the resultant constants are not consistent with those predicted by computational methods. An alternative explanation involving a non planar geometry, consistent with the results of computational methods is favoured.

Pursuing the rotational spectra of large molecular systems

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In a quest for studying large molecular systems two new configurations using laser-ablation coupled with narrowband molecular beam and broadband chirped pulse Fourier-transform microwave techniques (LA-MB-FTMW and LA-CP-FTMW) have been configured and tested in our group. The current experimental set ups have been optimized to record the rotational spectra at low frequency ranges in the 2–8 GHz region. A detailed description of the experimental systems as well as improvements in the data acquisition routines will be presented. The present state-of-the-art of microwave spectroscopy is paving the way towards the study of larger, more complex, biological systems which have been previously considered as being out of reach of high-resolution spectroscopic studies.

Acknowledgments: The authors thank the financial fundings from Ministerio de Ciencia e Innovación (Consolider-Ingenio 2010 CSD2009-00038 program "ASTROMOL", CTQ2013-40717-P and CTQ2016-76393-P), Junta de Castilla y León (VA077U16) and European Research Council (FP/2007-2013) / ERC-2013- SyG NANOCOSMOS, are gratefully acknowledged. E. R. A. thanks Ministerio de Ciencia e Innovación for FPI grant (BES-2014-067776) and I.L.O. thanks Junta de Castilla y León for a postdoctoral contract.

Exploring the generation of new species using laser ablation Fourier transform microwave spectroscopy techniques: the study of N-carbamoyl glycine

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Santiago Mata¹, José L. Alonso¹

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At the University of Valladolid, substantial advances in laser ablation procedure had made possible to transfer many thermally fragile molecules into the gas phase and to probe their rotational signatures in the isolated conditions of a supersonic expansion by Fourier transform microwave techniques.^{1,2} Very recently, we have successfully applied these techniques to the generation and spectroscopic characterization of glycinamide³ and hydantoin,⁴ possible precursors of glycine. During the investigation of related acyclic hydantoic acid (N-carbamoyl glycine), for which three different conformers have been unveiled, we surprisingly observed the formation of cyclic hydantoin, glycine, urea, methyl isocyanate, and other known astrophysical species. Among the numerous unassigned lines in the spectra, cyclic glycine N-carboxyanhydride has been detected for the first time. Present results open new ways towards the generation and spectroscopic characterization of new chemical species using a laser ablation source coupled with high-resolution Fourier transform microwave techniques.

Acknowledgments: The authors thank the financial fundings from Ministerio de Ciencia e Innovación (Consolider-Ingenio 2010 CSD2009-00038 program "ASTROMOL", CTQ2013-40717-P and CTQ2016-76393-P), Junta de Castilla y León (VA077U16) and European Research Council (FP/2007-2013) / ERC-2013- SyG NANOCOSMOS, are gratefully acknowledged. E. R. A. thanks Ministerio de Ciencia e Innovación for FPI grant (BES-2014-067776)

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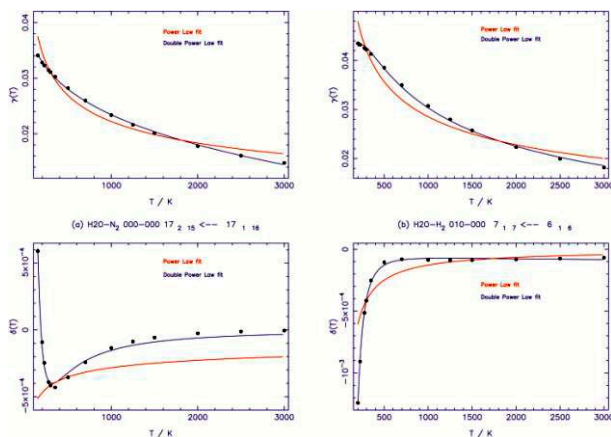
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On the temperature dependence of half-widths and line shifts for molecular transitions in the microwave and infrared regions

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An expression was developed that correctly models the temperature dependence of the half-width over large temperature ranges and the temperature dependence of the line shift, even for cases where the line shift changes sign. The expression was derived from the expansion of the collisional cross-sections in a series of powers of the relative velocity of the radiator and perturber. Cutting off at two terms yields a complex double power law (DPL) expression, where the real and imaginary parts describe the temperature dependence of the half-width and line shift, respectively. Data were collected for more than 100 thousand transitions and the standard power law expression for the half-width and line shift were compared with the new double power law expression. It is shown that the double power law works well for all transitions, even those that exhibit unusual structure, which the standard power law cannot model. The DPL expression gives better results than the standard power law for all transitions studied and the DPL model gives good results for the temperature dependence of the line shift when it changes sign. The figure below shows examples of power law and double power law fits to 2 transitions: the $17_{215} \leftarrow 17_{118}$ rotation band transition of H_2O in collision with N_2 and the $7_{17} \leftarrow 6_{16}$ ν_2 band transition of H_2O in collision with H_2 . The DPL model for the temperature dependence of the line shift was compared with the linear model, which is currently used on the HITRAN database. In all cases the DPL model gave much better results than the linear model no matter what temperature range was considered. The new formalism allows a substantial reduction in the number of parameters that need to be stored in databases and the same expression can be utilized in radiative transfer and simulation codes for both the half-width and line shift.



Calculation of half widths and line shifts of $\text{H}_2\text{O}-\text{N}_2$ collision system using the modified complex Robert–Bonamy formalism

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Water vapor is the principal absorber of infrared radiation in the Earth's atmosphere. Knowing the line shape parameters for water vapor is crucial to understanding remote sensing measurements. In this work, semi-classical line shape calculations using the Modified Complex Robert–Bonamy (MCRB) [1,2] formalism were performed to determine the half-width (γ) and the line shift (δ) for the $\text{H}_2\text{O}-\text{N}_2$ collision system at several temperatures. The MCRB calculations use an exact trajectory model [3], include all complex terms, a potential composed of electrostatic, atom–atom (expanded to 20th order and 4th rank), London dispersion and induction components, and explicit integration of the velocity integral. While most parameters in the potential are well known, the coefficients of the atom–atom potential need to be adjusted to reproduce a set of well-chosen half-width and line shift data.

The data were selected by applying an intercomparison procedure on the experimental $\text{H}_2\text{O}-\text{N}_2$ database (8235 transitions). These data were further refined by applying the Group of Transition rules (family of transitions [4] and Ma's rules [5]). First, the variation in the half-width as a function of atom–atom coefficients was studied. Then, changes are made to the atom–atom coefficients, new MCRB calculations made, and the calculated half widths and line shifts are compared to the experimental data. This procedure is iterated until the final standard deviation of the percent difference between the selected data and calculated data are a minimum.

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High accuracy ab initio DMS and extra high accuracy PES for sub-percent calculation of line intensities

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C4.3

Calculation of rotation–vibration line intensities with sub-percent accuracy has recently become a standard requirement for the applications in retrieval and monitoring of gases in the Earth's atmosphere and potentially in the atmospheres of exoplanets. A major factor in the accurate calculation of line intensities is the requirement for the high accuracy ab initio Dipole Moment Surface (DMS) (e.g. references [1,2]). We present here the newly developed DMS surfaces for H₂O [3], HCN [4] and O₃ [5] molecules and the results of the line intensities calculations using these surfaces.

In this talk we also demonstrate that the change from "good" potential energy surface (PES) to "excellent" PES, used for the line intensities calculations is also very important. Sometimes the change in intensities reach up to 1 or 2 percent. By "good" we mean here, for example, the PES with a standard deviation of 0.025 cm⁻¹ [6] and by "excellent" the PES with the standard deviation 0.011 cm⁻¹ [7]. Details of studies on H₂O [3], O₃ [5], HCN [4] and CO₂ [2] molecules will be presented in the talk.

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Line shape parameters from first principles: investigation of the S and O branches in the H₂-He system

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Hydrogen molecule is the most abundant molecule in the Universe. It is investigated in various physical fields, ranging from astrophysics and the analysis of gas giants' atmospheres [1,2], to ultra-accurate measurements in molecular spectroscopy [3,4,5], and even in the search for physics beyond Standard Model [6]. Recently [7] it was pointed out, that the available data regarding the line-shape parameters of hydrogen is rather sparse. The development of experimental techniques in molecular spectroscopy requires a sub-percent accuracy of the theoretical calculations. It is believed that fully quantum calculations, based on the close-coupling scheme, could fulfill such requirements.

The collisional system of hydrogen molecule and helium atom is a perfect benchmark system for performing complex, *ab initio* investigation line-shape parameters. It involves only four electrons, allowing researchers to calculate the potential energy surface of such system with highly accurate methods of quantum chemistry. Moreover, because of the small mass of the system and large rotational constant of the hydrogen molecule, the dynamical calculations can be performed in reasonable computational time.

Using the recently reported ultra-accurate potential energy surface for the H₂-He system [8], we performed close-coupling calculations of generalized cross sections for lines of the S and O branches. We investigated 60 lines in total, for vibrational bands from 0-0 to 0-5 and rotational levels up to $j=5$. Generalized spectroscopic cross sections were obtained from S-matrix elements for a wide range of kinetic energies (from 0.1 to 9000 cm⁻¹). The cross sections were later averaged over the relative speed distribution of the colliding pair, leading to the final line-shape parameters: pressure broadening and shifting coefficients and real and imaginary part of the Dicke contribution to the Hess profile. The parameters are obtained for 17 temperatures, ranging from 5 to 2000 K. This is the first complex investigation of the S and O branches in the H₂-He system using *ab initio* methods.

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Spectroscopic databases for the VAMDC and dat@osu portals

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A5.1.

Dijon spectroscopic databases include calculated line lists, in positions and intensities, that are obtained from experimental spectroscopic analyses. They contain 6 molecules: CH₄, C₂H₄, CF₄, SF₆, GeH₄ and RuO₄ and are all compatible with the XSAMS (XML Schema for Atoms, Molecules, and Solids) format adopted with the Virtual Atomic and Molecular Data Centre (VAMDC) Project (<http://www.vamdc.org>). VAMDC, a worldwide consortium which federates atomic and molecular databases through an e-science infrastructure, aims to provide a unique access point for scientists seeking the best atomic and molecular data for their studies. So far, development of new tools allows to easily download and compare data issued from different databases in a single XML document or into the HITRAN2004 format. Making the comparison that easy will help data users in the choice of data that best match their needs. It will also help data producers by checking the consistency of their data.

All these databases can be accessed either directly or through the VAMDC portal (<http://portal.vamdc.org>) and are also referenced through the dat@osu portal which aims to reference all research databases in the Bourgogne Franche-Comté region (<https://dataosu.obs-besancon.fr>).

Computing spectra of open-shell diatomic molecules with duo

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Duo [1] is a program designed to solve a coupled Schrödinger equation for the motion of nuclei of a given diatomic molecule characterized by an arbitrary set of electronic states. Duo is capable of both refining potential energy curves (by fitting data to experimental energies or transition frequencies) and producing line lists. Our most recent results of applying Duo to produce hot line lists for open-shell diatomic molecules include NO [2], SiH [3], PO and PS [4], C₂ [5], SN and SH [6] and AlH [7]. The line lists for TiO, MgO and YO are in progress. The published version of Duo only considers truly bound states. We are now working on extending Duo to treating quasi-bound or resonance states, or indeed the continuum itself, using the stabilization method. As an illustration, we present simulations of spectra of the quasi-bound A ¹Π – X ¹Σ⁺ system of AlH and of the continuum system A ¹Π – X ¹Σ⁺ and B ¹Σ⁺ – X ¹Σ⁺ system of NaCl.

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Accurate CO₂ Raman spectral simulation: an algebraic alternative based on anharmonic ladder operators

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A53

The origin of this algebraic spectral analysis approach comes from the vibron model, which was devised to describe phenomenologically the nuclear motion of diatomic and polyatomic molecules [1–3]. The vibron model consists in proposing a unitary group as a dynamical group to model the vibrational (or rovibrational) Hamiltonian as an expansion in terms of its generators taking into account anharmonicities from the outset. A major problem of the model was that a link between Hamiltonian parameters and force constants did not exist and the resolution was far from the experimental accuracy. Since then, the algebraic approaches have evolved and nowadays a clear connection between the spectroscopic parameters and the force constants has been established (see e.g. [4]), providing predictions with spectroscopic accuracy (see e.g. [5–8]). This progress has permitted to simulate the CO₂ Raman spectrum [9], which has allowed us to identify new experimental vibrational bands [10].

In this presentation we show the recent results of a polyad-preserving algebraic approach to molecular structure applied to carbon dioxide in its ground electronic state. This approach has allowed us to reproduce 178 experimental data set of vibrational energies up to 26550 cm⁻¹ making use of the three most common polyad schemes for this molecular species [11]. The results are comparable to those obtained with variational procedures, where a polyad number is not preserved, based on phase-space Hamiltonians [12]. In addition, we present the spectral analysis of the experimental Raman spectrum [13] based on this algebraic approach. This has permitted to assess the quality of the wave functions with respect to the previous study [10].

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Chiral rotational spectroscopy

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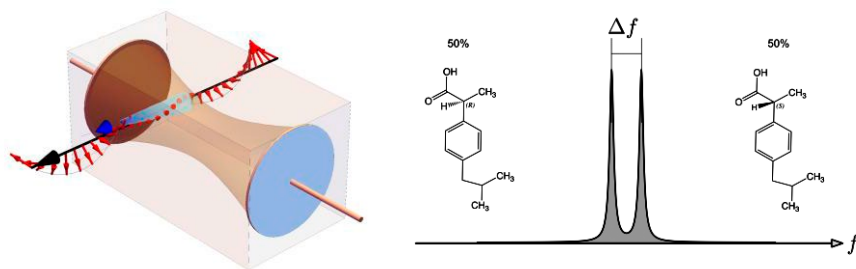
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We present the theoretical foundations of chiral rotational spectroscopy, a technique that enables the determination of the orientated optical activity pseudotensor components B_{xx} , B_{yy} and B_{zz} of chiral molecules, in a manner that reveals the enantiomeric constitution of a sample and provides an incisive signal even for a racemate. The basic property of a chiral molecule that is probed in typical optical rotation experiments using fluid samples is the isotropic sum of the electric-dipole / magnetic-dipole polarisability. The ability to determine orientated rather than isotropically averaged chiroptical information, in particular the individual optical activity polarisability components is highly attractive, as these offer a wealth of information about molecular chirality which is only partially embodied by the isotropic sum.

Our technique is based on illuminating molecules with circular polarised light (see Fig. 1) inducing oscillations in the charge and current distributions of the molecule, biasing the rotation of the molecule while shifting its energy in an orientationally and chirally sensitive manner. Such shifts constitute our orientated chiroptical response

Chiral rotational spectroscopy could find particular use in the analysis of molecules that are chiral solely by virtue of their isotopic constitution and molecules with multiple chiral centers. Our proposed technique offers the more familiar polarizability components α_{xx} , α_{yy} , and α_{zz} as by-products, which could see it find use even for achiral molecules.



Proton transfer tunneling splittings and the imaginary mode Hamiltonian: the beginning of a beautiful friendship

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Theoretical methods can be very useful in the interpretation of experimental observables, as for instance tunneling splittings. Here, we concentrate on semiclassical or quantum methods that can deal with tunneling splittings emerging from proton transfer reactions in symmetric systems. To perform this type of theoretical studies we propose the use of the imaginary-mode Hamiltonian (iMDH)[1], which is formulated in terms of the (mass-weighted) normal mode coordinates of the transition state for reaction.

iMDH is multidimensional (as is the nature of the quantum mechanical tunneling), and assumes that the normal modes perpendicular to the reaction coordinate (taken as the mode of imaginary frequency at the transition state) can be separated into enhancing (or symmetric modes), suppressing (or antisymmetric modes) and non-contributing (or undisplaced) modes. The reaction coordinate is a symmetric double well potential, whereas the rest of the normal modes are represented by harmonic oscillators linearly coupled to the reaction coordinate.

In some cases the iMDH was directly implemented in the semiclassical approximated instanton method, whereas in other cases we preferred to carry out a direct diagonalization. The iMDH allowed us to successfully calculate ground-state, as well as vibrationally excited tunneling splittings in several molecules with single or multiple proton transfer. Examples are: malonaldehyde, formic acid dimer, porphycene and the vinyl radical.

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High-resolution rotational spectroscopy of 3-Methylbutyronitrile – a molecule of astrophysical interest

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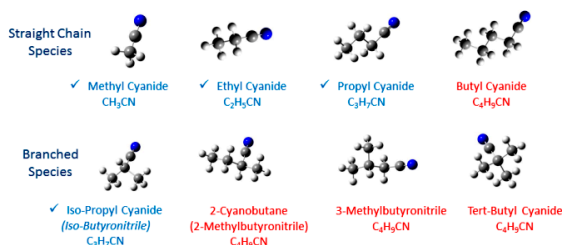
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We present high-resolution rotational spectra of the two conformers of 3-methylbutyronitrile (C_4H_9CN), i.e., the gauche and anti-conformer.

The molecule is one of the structural isomers of butyl cyanide (C_4H_9CN). Smaller straight-chain species, such as methyl cyanide, ethyl cyanide and propyl cyanide, as well as the branched-chain species iso-propyl cyanide, have already been identified in space successfully. However, despite the fact that laboratory spectra of the straight-chain n-butyl cyanide conformers have been analysed, the molecule has not been detected in space up to now (Ordu et al. 2012). More recent simulations predict the abundance of n-butyl cyanide just short of the detection limit of previous ALMA observations. The abundances of 3-methylbutyronitrile (and 2-cyanobutane, another structural isomer) discussed here are predicted to be higher than the abundance of n-butyl cyanide (Garrod et al. 2017).

Here, we present spectra between 2 and 24 GHz that were obtained by means of Fourier transform microwave spectroscopy. Spectra between 36 and 403 GHz were recorded by means of frequency modulated (FM) absorption spectroscopy. The analysis yields precise rotational constants and higher order distortion constants, as well as a set of ^{14}N nuclear electric quadrupole coupling parameters for each of the two conformers. In addition, quantum chemical calculations were performed in order to assist the assignments. Frequency calculations yield insight into the vibrational energy structure, from which partition functions and vibrational correction factors are determined. These factors are used to determine experimentally and computationally the energy difference between the two conformers, which is revealed to be negligible.

Overall, this study provides precise spectroscopic constants for the search of 3-methylbutyronitrile in the interstellar medium. In particular, this molecule is a perfect test case for our knowledge of branched molecule formation in space.



In blue: Molecules which were identified in space. Most molecules are straight-chain species, besides iso-propyl cyanide. In red: Molecules which are currently searched for in ALMA spectra.

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Solving discrepancies between theory and experiment: Methyl Jasmonate and Zingerone

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B5.2:

Modern structural studies of biologically relevant molecules require an exhaustive interplay between experiment and theory. In this work, we will present two examples where a poor choice of the theoretical method led to a misinterpretation of experimental results. We do that by performing a rotational spectroscopy study on two flexible and moderate-large sized biomolecules: Methyl jasmonate and Zingerone. The spectra for those two molecules were recorded in the 6–18 GHz frequency region was collected in the CP-FTMW spectrometer available at the University of the Basque Country (UPV/EHU).[1] The internal rotation splitting due to the potential barrier were analyzed and fit using the XIAM code[2] and the BELGI-C₁[3]. Two conformers were observed for methyl-jasmonate and one conformer for zingerone. Clearly, not every theoretical method is able to predict correctly the conformers observed. Only methods taking into account the dispersion effects and the balance between weak hydrogen bonds can achieve that goal. The results shown in this work prove thus the key role of rotational spectroscopy as a benchmark to evaluate the performance of theoretical methods.

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Polyalcohols as artificial sweeteners: signs of a sweetness–structure connection

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Since early last century, abundant research has addressed the link between sweetness and the structure of sweeteners. None of these theories has been able to offer a unified explanation regarding the sweetness–structure relation until Shallenberger and Acree's proposal.^{1,2} They observed that the sweetness depends on the strength of two H-bonds by which the sweetener is bound to the sweet receptor. They established that one of the two electronegative atoms might act as a proton donor (AH) in the hydrogen bond interaction and the other as acceptor (B). These two groups form what is called the *glucophore*, which refers to the part of the sweetener that interacts with the sweet receptor. Microwave spectroscopy studies of some molecules belonging to the polyalcohol family (sorbitol, dulcitol, mannitol, erythritol, etc.) have been carried out by means of broadband microwave spectroscopy techniques³ in combination with a laser ablation technique for vaporize the sample.⁴ The structural characterization in isolation conditions of these molecules gives us valuable information to contrast with the postulated theories about the sweet taste, deepening in the origin of the sweet properties of these molecules.

Acknowledgements: The authors thank the financial fundings from Ministerio de Ciencia e Innovación (Consolider-Ingenio 2010 CSD2009-00038 program "ASTROMOL", CTQ2013-40717-P and CTQ2016-76393-P), Junta de Castilla y León (VA077U16) and European Research Council (FP/2007-2013) / ERC-2013- SyG NANOCOSMOS, are gratefully acknowledged. E. R. A. thanks Ministerio de Ciencia e Innovación for FPI grant (BES-2014-067776)

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Microwave spectroscopic and quantum chemical investigations on 2-Acetylthiophene

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B5.4.

The torsional barrier of the acetyl methyl group strongly depends on the substituent attached to the other side of the carbonyl group, especially if double bonds or π conjugated systems are present. Although several molecules of this type have been investigated, no apparent trends for the torsional barrier of the acetyl methyl group have been found. In allyl acetone the barrier height is 224.95(120) cm^{-1} [1], while completely different values were found for *syn*- and *anti*-methyl vinyl ketone (376.6(2) cm^{-1} and 433.8(1) cm^{-1}) [2] or the *cis* and *trans* conformers of 2-acetyl-5-methylfuran (212.71(30) cm^{-1} and 307.78(59) cm^{-1}) [3]. In this work the influence of thiophene, a sulfur-containing five membered aromatic ring, on the internal rotation barrier will be presented.

The microwave spectrum of 2acetylthiophene was recorded using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2 to 26.5 GHz. The assignment of the transitions is currently in progress. Conformational analysis was carried out at the MP2/6-311++G(d,p) level of theory and yielded two stable conformers (*cis* and *trans*), whereby *cis*-2acetylthiophene is the energetically more stable conformer. The calculated torsional barrier at different levels of theory varies from 191 to 318 cm^{-1} and 160 to 284 cm^{-1} for the *cis* and the *trans* conformer, respectively. Coupled with the internal rotation, an oscillation of the acetyl group occurs with an amplitude of 5° for the *cis* and 10° for the *trans* conformer.

Calculations on several derivatives were also performed to compare the results of 2-acetylthiophene. We found that like 2-acetylthiophene all derivatives have two stable conformers. The comparison with 2-acetylfuran and 2-acetylpyrrole has shown, that the relative stability of the *cis* or *trans* conformer depends on the hetero atom in the ring. Further comparisons with the aldehyde derivatives 3-methyl-2-thiophenecarboxaldehyde, 3-methyl-2-furaldehyde and 3-methylpyrrole-2-carboxaldehyde have been drawn.

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Structure and rotational spectral features of *N*-Butyraldehyde oxime: a study using MB-FTMW

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n-Butyraldehyde oxime ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{NOH}$) has two geometrical forms with respect to the C=N bond, (*E*)- and (*Z*)-isomers. Values of C-C=N-O dihedral angle are 180 and 0 degree for (*E*)- and (*Z*)-isomers, respectively. Furthermore, this molecule has the possibility to exist in various rotational conformations in the gas phase, because of having a long flexible carbon chain with three C-C single bonds.

We have been observed the microwave spectra of *n*-butyraldehyde oxime from 26–40 GHz. Four rotational conformers were found to exist in the gas phase by Stark-modulated microwave spectroscopy (Stark-MW). They are the E_a and E_b conformers of (*E*)-isomers; the Z_a , and Z_b conformers of (*E*)-isomers. Rotational constants were determined for E_a , Z_a , and Z_b conformers. However, the data fitting was not succeeded for the E_b conformer due to the lack of experimental spectral lines.

Molecular structure and conformations of the (*Z*)-isomer of *n*-butyraldehyde oxime by gas-phase electron diffraction (GED). We have the results of the two types of data analysis. One is the GED+MW joint analysis, a combination of the GED data and two sets of rotational constants for the Z_a , and Z_b conformer. Another is the GED data analysis in the 2D large-amplitude motions for C-C the bonds.

In this work, we observed the rotational spectrum *n*-butyraldehyde oxime by molecular-beam Fourier transform microwave spectrometer. Our interests are: 1) determination of the rotational constants by high-resolution spectrum; 2) hyperfine splittings due to the ^{14}N atom; 3) search for the fourth conformer, the E_b conformer; 4) spectral assignments of the isotopomers; and 5) splitting lines due to the large-amplitude vibrational motion of the molecule. In the lower spectral range, 5–24 GHz, we could easily observe the spectral lines for the E_a , Z_a , and Z_b conformers which were resolved to three components in each a-type R-branch transition. Now we are focusing our third agenda, identification of the fourth conformer.

Microwave spectrum and nuclear quadrupole structure analysis of the $\text{NH}_3\text{-N}_2$ van der Waals complex

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C5.1

The pure rotational transitions of the $\text{NH}_3\text{-N}_2$ van der Waals complex and its deuterated isotopologues ($\text{ND}_3\text{-N}_2$, $\text{NHD}_2\text{-N}_2$, $\text{NH}_2\text{D-N}_2$) have been observed in the frequency range of 6–26 GHz using chirped-pulse Fourier-transform microwave (CP-FTMW) technique. Complicated hyperfine structure due to three quadrupole ^{14}N nuclei was resolved and examined for the first time, thus supplementing the previous pure rotational analysis of the only main isotopic species of $\text{NH}_3\text{-N}_2$ [1, 2, 3]. In the earlier papers [2, 3] six series of the millimeter-wave transitions have been assigned to the $K = 0$ or $K = 1$ states of the complex involving all combinations of the nuclear spin isomers of the parent molecules, *ortho/para*-ammonia and *ortho/para*-nitrogen. In our study one of the two detected $K = 0$ series belongs to already known ground state of the *ortho*- NH_3 -*ortho*- N_2 spin isomer [1–3], while another $K = 0$ series assigned to the *para*- NH_3 -*para*- N_2 spin isomer was not reported before. Two other $K = 0$ series were expected for *para*- NH_3 -*para*- N_2 and *para*- NH_3 -*ortho*- N_2 from earlier analysis [2], but current experiment calls their assignment into question. The hyperfine splitting patterns for all observed isotopic and nuclear spin species were examined in order to obtain the dynamical information about the orientation of the ammonia and nitrogen units within the van der Waals complex.

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New millimeter-wave study of the CO–N₂ van der Waals complex

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Recently, new CO–N₂ intermolecular potential energy surface has been carried out at the explicitly correlated coupled cluster level of theory with single, double, and perturbative triple excitations [1]. The accompanying bound state computations resulted in further progress in assignments of the measured rotational spectra of the CO–N₂ complex. Guided by these *ab initio* calculations a new millimeter-wave survey in the frequency range of 100–145 GHz was performed using the intracavity OROTRON jet spectrometer described elsewhere [2]. Newly observed lines were assigned to the *P*- and *R*-branches of the $K = 0 - 0$ subband correlating with the $j_{\text{CO}} = 2 - 1$, $j_{\text{N}_2} = 0$ internal rotor states of the CO–*ortho*N₂ nuclear spin modification. Experimental transitions with partly resolved hyperfine splitting due to nuclear spins of two ¹⁴N atoms were analyzed in order to determine the molecular parameters and structure of the complex in the $K = 0$, $(j_{\text{CO}}, j_{\text{N}_2}) = (2, 0)$ state detected for the first time.

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Microsolvation of ethyl carbamate conformers: a rotational spectroscopy study

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The microwave spectra of complexes between ethyl carbamate and up to three molecules of water generated in a supersonic expansion have been studied using both a chirped-pulse and a molecular beam spectrometers covering the 2–13 GHz frequency range. The monomer of ethyl carbamate shows an equilibrium in the gas phase between two close in energy conformations connected by a low interconversion barrier.[1, 2] The observation of these forms and their correspondent complexes depends on the carrier gas used due to collisional relaxation in the supersonic jet. While using argon only the most stable form and its complexes are observed, using neon both forms and their corresponding complexes can be observed. The structures of six new complexes have been characterized and in all cases water closes sequential cycles with the H–N–C=O amide group. They show a remarkable similarity in both structure and dynamics to those observed in related systems, as for example in formamide–(H₂O)_n clusters.

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Study of the molecular structure and microsolvation (H_2O $N=1-3$) of 2-Phenylpyridine by rotational spectroscopy

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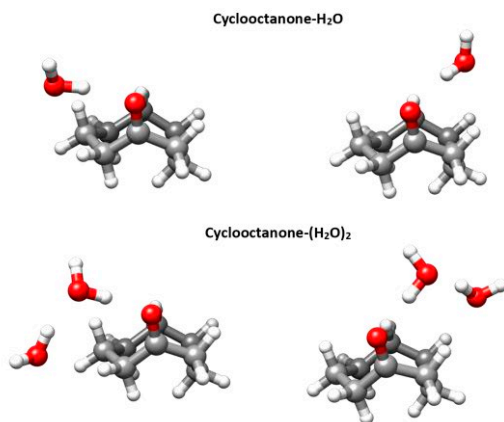
Conjugated organic ligands are usually used in devices as light emitting diodes or semiconductors due to their electronic and optical properties associated to its structure. One of the most employed conjugated organic ligand is 2-phenylpyridine (2ppy). We present the study of this molecule and its complexes with n water molecules ($n=1-3$) by rotational spectroscopy using a molecular beam Fourier transform microwave spectrometer (MB-FTMW) and a chirp pulse Fourier transform microwave spectrometer (CP-FTMW). For the monomer and the one water complex we have also assigned all their ^{13}C and ^{15}N single isotopologues in their natural abundance. These measures have enabled a direct structural comparison between the bare molecule and its water complex, determining not only the structure of 2ppy but also how the water affects to it.

Structures of the complexes of Cyclooctanone with water

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Water is present in the air with a concentration of up to 4 %, and also in the olfactory mucosa, where it has the role of protecting the olfactory epithelium. Odorants are thus very likely to interact with water before reaching the receptor, which may affect their conformational properties or even produce a reaction. The study of complexes of cyclooctanone with water constitutes a first step towards understanding how larger macrocyclic compounds interact with water before they reach the olfactory receptors. Two complexes of the most abundant conformer of cyclooctanone with one water molecule, and two complexes with two water molecules have been characterised using chirped-pulse Fourier Transform Microwave (CP-FTMW) spectroscopy. The observation of all ¹³C and some ¹⁸O isotopic species of the cyclooctanone ring in the complexes in their natural abundances, and of the ¹⁸O species of the water molecules using isotopically enriched water allowed us to calculate the substitution structures of the complexes. These have been compared with the effective structures of the complexes and with that of cyclooctanone to determine any changes undergone by cyclooctanone upon complexation. In the cyclooctanone-H₂O complexes, water forms a O-H...O hydrogen bond with the carbonyl oxygen of cyclooctanone and two O...H-C hydrogen bonds with the -CH₂ groups in the cyclooctanone ring. In the cyclooctanone-(H₂O)₂ complexes, the second molecule of water binds primarily to the first molecule of water through hydrogen bonding, whilst also forming secondary interactions with the -CH₂ groups in the ring.



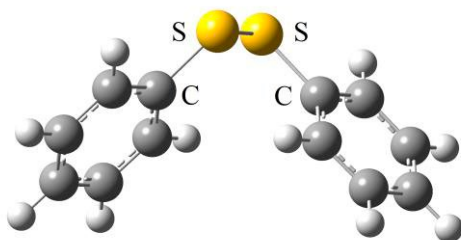
Microwave spectrum and equilibrium structure of Diphenyl Disulfide

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The disulfide bridge ($-S-S-$) is an important structural motif in organic and protein chemistry, so the determination of accurate equilibrium structures is well justified. Diphenyl disulfide ($C_6H_5-S-S-C_6H_5$, DPDS, see figure) is widely used in organic synthesis and a challenging target since its structure is determined by 34 independent parameters. We report supersonic-jet microwave measurements of the rotational spectra of DPDS (including all ^{13}C and ^{34}S isotopologues) and the determination of the equilibrium structure by the mixed estimation (ME) method. A single conformer of C_2 symmetry was observed in the gas-phase. In order to estimate the equilibrium structure of this conformer, the mass-dependent r_m method was used to fit the structural parameters concurrently to predicate parameters and moments of inertia, affected with appropriate uncertainties. The predicate parameters were obtained by high-level quantum-chemical computations. A careful analysis of the results of different fits and a comparison with the ab initio optimizations confirms the validity of the used methods. The most interesting part of the structure of DPDS is the $S-S$ bond. The $r(S-S)$ bond length at 2.020 Å is very similar to the value found in $HSSH_{anti}$ (2.022 Å) but significantly shorter than in CH_3SSCH_3 (2.033 Å). The $r(C-S)$ bond length at 1.776 Å is rather short. The bond angle $C-S-S$ is 105° (102.1° in CH_3SSCH_3). The dihedral angle $\tau(C-S-S-C)$ at 82.6° shows differences with previously known values (CH_3SSCH_3 : 84.8° , $HSSH_{anti}$: 90.6° ; in $HSSOH_{anti}$ 84.8° and in $HSSOH_{syn}$ 99.4°). Finally, the deformation of the benzene ring is also worthy of note. Full structural details will be reported at the Conference.



Semi-experimental structure of vinyl acetate determined by microwave spectroscopy and ab initio methods

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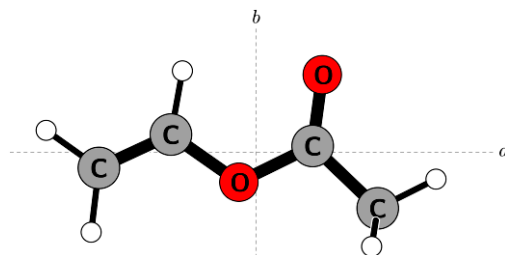
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A6.2

Vinyl acetate is a well-known molecule in the field of gas-phase spectroscopy. For example Velino et al. (2009) [2] and Nguyen et al. (2014) [1] show transitions in the frequency region from 64 to 78 GHz [2] and 7 to 37 GHz [3] respectively. Kolesniková et al. (2015) [3] further investigated the existence of vinyl acetate in the interstellar area of Orion KL. The presented project is the first to aim for accurate structure determination from isotopologue data of vinyl acetate.

The microwave spectrum of vinyl acetate was investigated in the region from 8.3 to 27.3 GHz using the IMPACT (in-phase/quadrature-phase-modulation passage-acquired-coherence technique) spectrometer [4]. Higher resolution measurements in areas of interest were carried out with the CO-BRA-FTMW (multioctave coaxially oriented beam-resonator arrangement Fourier-transform microwave) spectrometer [5]. Vinyl acetate contains a methyl group and its internal rotation couples to the overall rotation which leads to notable splittings in the rotational spectrum. The fit of molecular parameters to the experimental spectrum was carried out utilising the XIAM [6] program assuming C_s symmetry.

Several of the strongest transitions of the parent molecule were observed for ^{13}C and ^{18}O isotopologues in natural abundance as well. From the rotational constants of the isotopologues and with the help of ab initio methods the semi-experimental equilibrium structure of vinyl acetate was determined.



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Pure rotational spectrum of ^{15}ND and isotopic-independent Dunham-type analysis of imidogen radical

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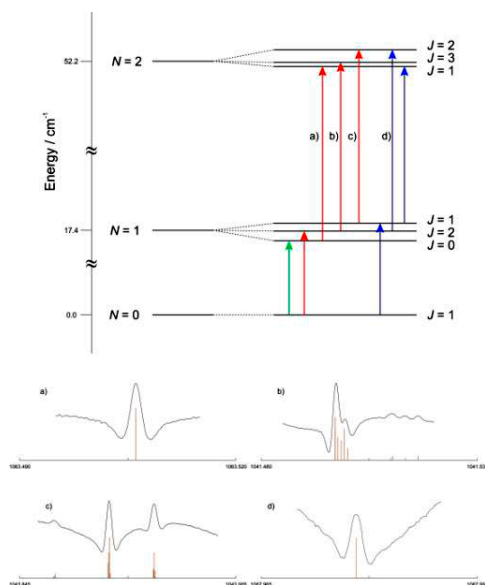
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The rotational spectrum of ^{15}ND in its ground electronic $X^2\Sigma^-$ state has been recently observed in the Bologna laboratory.

The radical has been generated in a glow discharge of a mixture of $^{15}\text{N}_2$ and D_2 in Ar as a buffer gas. Thirty-four hyperfine components belonging to the ground vibrational state and 9 components for the $v = 1$ state have been recorded with a frequency-modulation millimetre-/submillimetre-wave spectrometer. They include the complete fine-structure of the $N = 1 \leftarrow 0$ transition and the strongest fine-components of the $N = 2 \leftarrow 1$ transition for the ground state (see Figure 1), and the $\Delta J = 0, +1$ components of the $N = 1 \leftarrow 0$ transition for the $v = 1$ state.

These new isotopic measurements complete the high-resolution spectroscopy characterisation of the imidogen radical: presently, all four stable isotopologues, i.e., NH , ND , ^{15}NH and ^{15}ND , have been studied in the millimetre, and/or infrared domains. The resulting, extensive data set have been analysed using a multi-isotopologue Dunham model to represent the ro-vibrational, fine, and hyperfine energy contributions. The least-squares fit was performed on a sample of more than 1500 transitions, yielding a comprehensive set of isotopically independent U_{lm} parameters plus 13 Born-Oppenheimer Breakdown coefficients Δ_{lm} . As alternative approach, we performed a Dunham analysis in terms of the most abundant isotopologue coefficients Y_{lm} and some isotopically dependent Born-Oppenheimer Breakdown constants δ_{lm} [R. J. Le Roy, *J. Mol. Spectrosc.* **194**, 189 (1999)]. The two fits provide results of equivalent quality.

The Born-Oppenheimer equilibrium bond distance for imidogen radical has been calculated yielding $r_e^{\text{BO}} = 103.606721(13)$ pm and the zero point energies have been derived for all isotopologues. Additionally, the adiabatic correction to the equilibrium distance have been determined from purely experimental data and compared to a value estimated using high-level *ab initio* calculations.

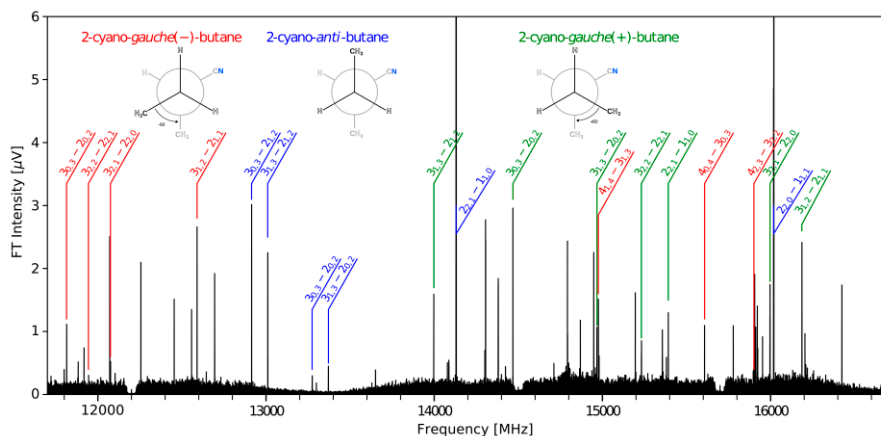


Rotational spectroscopy of the two higher energy conformers of 2-cyanobutane

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Stephan Schlemmer¹

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We present high-resolution rotational spectroscopy of two out of three conformers of 2-cyanobutane. Spectra were taken between 10–26 GHz by means of chirped-pulse spectroscopy. Spectra between 36 and 402 GHz were recorded by means of frequency modulated (FM) absorption spectroscopy. The analysis yields precise rotational constants and higher order distortion constants, as well as a set of ¹⁴N nuclear electric quadrupole coupling parameters. In addition, quantum chemical calculations were performed assisting the assignments. Calculations of vibrational frequencies yield insight into the vibrational energy structure from which partition functions and vibrational correction factors are determined. These are used to determine experimentally and computationally the energy difference between the conformers. Overall, this study provides precise spectroscopic constants for the search of 2-cyanobutane in the interstellar medium. In particular, this molecule appears as an interesting case to test our knowledge of (branched) molecule formation in space.



Precise lamb-dip studies of monodeuterated Methanol

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We report on the results of precise frequency and hf constants measurements of CH₂DOH and CH₃OD molecules performed with the sub-Doppler spectrometer of the the IAP RAS, N.Novgorod [1]. Due to Lamb dip technique, the experimental accuracy of the transition frequencies in the range 44–520 GHz is improved by more than two orders in comparison with conventional spectroscopy [2–5]. The obtained data are of great interest both in the studies of physical parameters in the regions of star formation, as well as in a search for possible m_e/m_p variations from comparison of laboratory and radio astronomical frequencies.

All laboratory measurements were performed thanks to the Russian Foundation for Basic Research (project 16-02-00761). Their analysis was supported by the Russian Science Foundation (project No.17-12-01256).

B6.1.

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State-to-state rotational rate coefficients for $\text{NH}_3\text{-NH}_3$ collisions obtained with pump-probe chirped-pulse experiments

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Relaxation of rotational state populations of ammonia is studied in the laboratory by pump-probe experiments and observing its inversion doublets in the ground vibrational state using a broadband chirped pulse Fourier transform microwave spectrometer. The thermal distribution of states is altered by a resonant pump pulse that changes the population of an inversion doublet of a single rotational state. The resulting deviation from equilibrium is then propagating to other states due to collisions and interrogated by a probe pulse. The bandwidth of the spectrometer allows to probe the intensity of many inversion transitions within a single chirped pulse excitation on sub-microsecond timescales as a function of the pump pulse conditions. The relaxation time of the radiation-induced superposition state of the two level tunneling system (T2) is inferred from the free induction decays (FID) of the individual states. Also the collisional relaxation time (T1) for the population difference of the two-level system is determined. These values exhibit a linear pressure dependence, the slope of which agrees very well with previous measurements 1,2,3,4.

Analysis of collision induced transitions observed in these pump-probe experiments reveals the well known hierarchy of collisional relaxation in ammonia which was first found by Oka fifty years ago through steady state intensity measurements⁵. Collision-induced transitions with dipole selection rules ($\Delta J = 0$) are faster than $\Delta J = \pm 1$ transitions. Of those only $\Delta K = 0$ transitions could be detected and are thus much faster than those with $\Delta K \neq 0$. State-to-state rates are obtained by simulations of all coupled states fitted to the temporal behavior of the complete pump probe experiments where many individual (J,K) rotational states can be addressed step by step by separate pump pulse sequences.

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Chirped-pulse millimetre-wave spectrometer for the 140–180 GHz region

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A chirped-pulse millimetre-wave spectrometer working in the 140–180 GHz range has been developed for spectroscopic investigations of molecules and clusters in pulsed supersonic expansions. Its sensitivity is illustrated by a measurement of the relative intensities of pure rotational transitions in $^{14}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ and $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ in a natural N_2O sample and of pure rotational transitions of the carbon monoxide dimer ($^{12}\text{C}^{16}\text{O}$)₂.

Wave-packet imaging spectroscopy of the nitrogen dimer

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B6.4.

Irradiation of a molecular system by a short pulse of electromagnetic wave creates a non-stationary state of motion, which is commonly termed quantum wave packet (WP). Since a WP is a coherent superposition of several eigenstates, the time-dependent observable provides information on the energy intervals between the constituent eigenstates. Several spectroscopic methods working in such a time domain have been developed and applied extensively so far.

Here we present another variation of time-domain molecular spectroscopy. In our approach, molecular WPs are created via impulsive Raman excitation by intense nonresonant ultrashort laser pulses. Then, another time-delayed (more) intense ultrashort pulse is irradiated onto the molecular system to induce "Coulomb explosion", which multiply ionizes the system and makes its prompt rapture into charged fragments. The resultant fragments are detected by a 2D ion-imaging setup newly constructed in the present laboratory [1,2]. By successively changing the delay between the excitation and the explosion, time-dependent kinetic-energy and angular distribution of the fragments is taken as a series of ion-image records.

For demonstrating the capability of the present experimental method, we have examined the dimer of nitrogen molecules. Since this cluster possesses no appropriate optical transition from MW to UV region, spectroscopic investigation so far reported is so scarce [3]. The adiabatically cooled cluster produced in a supersonic expansion was excited by a linearly polarized pulse, and N_2^+ fragments created by Coulomb explosion of the dimer were monitored. Signal of N_2^+ from much abundant monomer can be differentiated since the exploded N_2^+ has substantial kinetic energy and gives images well separated. The time-dependent fragment angular distribution shows complex oscillatory change in $\sim\text{ns}$ regime. This observed feature is attributed to WP propagation pertinent to overall cluster rotation. Fourier-transformation of the data shows several regular series of peaks in the power spectrum. They are assigned to rotational-level intervals for different internal-rotation manifolds. The assignment has been confirmed by conducting the measurement of the $^{15}\text{N}_2$ isotopic species. Rotational constants are obtained, yielding to the experimental determination of the intermolecular distance between the two nitrogen molecules. By examining with higher time resolution, faster ($\sim\text{sub ps}$) oscillation has been identified in angular distribution. This is most probably due to WP propagation pertinent to intermolecular vibration (or internal rotation). The present results will be valuable experimental input for elucidating geometry and internal dynamics of this cluster with fundamental importance.

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Infrared spectrum and intermolecular potential energy surface of the CO–O₂ dimer

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Only a few weakly-bound complexes containing the O₂ molecule have been characterized by high resolution spectroscopy, no doubt due to the complications added by the oxygen molecule's unpaired electron spin. Here we report an extensive infrared spectrum of CO–O₂, observed in the CO fundamental band region (2150 cm^{–1}) using a tunable quantum cascade laser to probe a pulsed supersonic jet expansion. The rotational energy level pattern derived from the spectrum consists of stacks of levels characterized by the total angular momentum, J , and its projection on the intermolecular axis, K . Five such stacks are observed in the ground vibrational state, and ten in the excited state ($v(\text{CO}) = 1$). There are two separate groups of stacks, with no observed transitions between them. The groups correspond to different projections of the O₂ electron spin, and correlate with the two lowest fine structure states of O₂, $(N, J) = (1, 0)$ and $(1, 2)$. The rotational constant of the lowest $K = 0$ stack implies an effective intermolecular separation of 3.82 Å, but this should be interpreted with caution since it ignores possible effects of electron spin. The experimental energy levels enable us to predict the microwave and millimeter wave spectra of CO–O₂.

A new high-level 4-dimensional potential energy surface is developed for CO–O₂, and rotational energy levels are calculated for this surface, ignoring electron spin. By comparing calculated and observed levels, it is possible to assign detailed quantum labels to the observed level stacks. The next step will be to include spin in the energy level calculation, which has not been done previously for a weakly-bound complex in which O₂ undergoes hindered rotation.

Production and study of ionic clusters by photodissociation spectroscopy

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Ionic clusters are defined as charged species A^+-L_n formed by the interaction between ions A^+ and neutral ligands L_n . These entities possess a binding energy ($10 - 10^4 \text{ cm}^{-1}$, i.e. $1.24 \times 10^{-3} - 12.5 \text{ eV}$), that lies between those of neutral clusters and those having the strongest chemical covalent bonds¹. Ionic clusters as ideal small controllable systems are important to the study of chemical reactions such as solvation processes and proton transfer². Furthermore, in the atmosphere, their condensation leads to aerosols formation that directly affect our climate³.

We will present our homemade instrument able to produce those complexes for study by high-resolution photodissociation spectroscopy. This instrument is essentially composed of (i) a pulsed supersonic expansion plasma source, to produce the desired species at low rotational temperature, (ii) a time of flight mass spectrometer which includes a single unit able to perform acceleration, bunching and gating⁴.

The first mass spectra of cationic and anionic clusters, formed from different gas mixtures, will be presented. Two different ionization methods will be compared including an electrical discharge and an electron gun. Finally, we hope to present the first photodissociation spectroscopic results.

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Unravelling non-covalent interactions in DNA-base ... Xanthine clusters

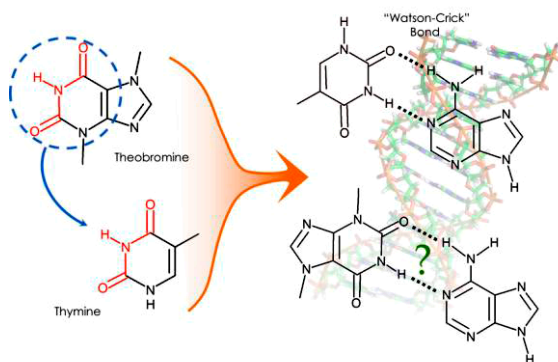
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Human metabolism commonly uses methylation processes as a tool for modulating gene expression, as changes in specific protein functions or as an epigenetic tool. In DNA, the methylation of a nucleobase immediately changes his ability for binding. Therefore, the study of the interactions between methylated bases sends light about how a structural modification changes the aggregation tendencies of DNA bases.

In the recent years, understanding the aggregation of DNA bases has been the goal of several studies, due to the relevance of such interactions for life[1,2]. However, the aggregation of DNA bases with other structurally similar compounds that are present in our metabolism, xanthine and its methylated derivatives has been rarely explored. The combination between these families is quite interesting, since some xanthines can create Watson-Crick links or analogue interactions [Fig. 1].

Here, we explore the interaction of adenine with different xanthines using a combination of mass-resolved spectroscopy and computational methods. A jet-cooled laser desorption system was used to obtain the isolated molecules and aggregates in a supersonic expansion. Next, the beam was explored using a combination of REMPI and IR/UV techniques to extract structural information. Comparison of such experimental results with the output from DFT calculations at M06-2X/6-31+G(d) and M06-2X/6-311++G(d,p) levels allowed us to assign the experimental spectra to a calculated structure. On the one hand, formation of these kind of aggregates tells us the aggregation preferences of purine bases; on the other hand, we can see the influence of the methylation in the intermolecular interactions and therefore, in the structure of the aggregates [Fig. 2].



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High-resolution spectroscopic study of the water-carbon dioxide van der Waals complex in the near-infrared range

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The jet cooled spectrum of $\text{H}_2\text{O}-\text{CO}_2$ and $\text{D}_2\text{O}-\text{CO}_2$ has been recorded in the 1.4 mm and 1.5 mm. range respectively by continuous-wave cavity ring-down spectroscopy. We observed three rotationally resolved b-type vibrational bands, two for $\text{H}_2\text{O}-\text{CO}_2$ and one for $\text{D}_2\text{O}-\text{CO}_2$. We assigned around 1000 lines in the case of $\text{H}_2\text{O}-\text{CO}_2$ and 120 lines for $\text{D}_2\text{O}-\text{CO}_2$. The vibrational assignment of those bands will be discussed but involves in terms of the (v_1, v_2, v_3) vibrational quantum numbers of the water monomer at least the $(1,0,1)$ for $\text{H}_2\text{O}-\text{CO}_2$ and the $(1,1,1)$ vibrational state for $\text{D}_2\text{O}-\text{CO}_2$. Even after vibrational excitation, the two vibrational bands of $\text{H}_2\text{O}-\text{CO}_2$ present tunneling splitting due to the internal rotation of the H_2O unit within the complex. This complex was studied before in the microwave [1] and mid-infrared [2] ranges. These studies and our work can be used to discuss the influence of vibrational excitation on internal rotation through tunneling mechanism. Finally the missing of one tunneling component for the vibrationally excited state of $\text{D}_2\text{O}-\text{CO}_2$ will be discussed.

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Universal behaviour of diatomic halo states and mass sensitivities of their properties

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A simple one-parameter scaling of the interaction potentials allows for a fairly close fitting of the wavefunctions of the corresponding diatomic halo states, reflecting thus the universality in the low-energy scattering of atoms. This universality means that all the parameters characterizing the diatomic halo states can be determined with high precision if one of these characteristics is accurately known. It can be applied to determine not only the scattering properties, but also their accurate mass sensitivities which appear eminently promising for probing the constancy of the proton-to-electron mass ratio.

A7.1.

High energy states of polyatomic molecules: application to hot spectra

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A7.2

Knowledge of accurate line positions and line intensities of various molecules and their isotopic species in wide spectral and temperature ranges is essential for the modelling of optical properties of planetary atmospheres, brown dwarfs and for other astrophysical applications. This implies reliable calculations of highly excited molecular energy states in large range of vibrational and rotational quantum numbers. The final aim is understanding of highly excited molecular states important for dynamics and construction of comprehensive lists of transitions based on accurate and extensive *ab initio* variational calculations for a large variety molecular species as for exemple CH₄ [1–4] PH₃ [5] C₂H₄ [6] SiH₄, CH₃F [7] GeH₄ [8] including all isotopologues and accounting for their symmetry properties. In case of elevated temperatures, quantum–mechanical calculations of ro–vibrational energy levels are very demanding and require a special attention, both in terms Hamiltonian/basis–set reduction [9,10] and data compression [11] to make calculations more feasible and final line lists lighter.

The TheoReTS database and information system [11] (<http://theorets.univ-reims.fr>, <http://theorets.tsu.ru>) developed by Reims and Tomsk groups for planetary and astrophysical spectroscopy applications will be briefly summarized, including examples on hot methane [12] and hot ethylene [13] data.

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Absolute vibrational assignment from fragmentary spectroscopic data in two isotopologues

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In this contribution we discuss application of the isotope effect to establish the absolute vibrational numbering in electronic states of diatomic molecules. This is illustrated by examples of single electronic states with various shapes of the potential curves (both regular and irregular) and states coupled by perturbations. The minimum number of spectroscopic data (either term values or spectral line positions) necessary to provide a unique numbering is considered. We show that at favourable conditions just four term energies (or spectral lines) in one isotopologue and one term energy in the other suffice.

Atmospheric oxygen mm-absorption: models review and uncertainties evaluation

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A7.4.

Molecular oxygen is one of the main atmospheric absorbers of millimeter-wave radiation. Oxygen molecule has a band around 60 GHz and a single spectral line at 118.75 GHz formed by fine structure magnetic dipole transitions within pure rotational triplets. "Zero-frequency" lines corresponding to the transitions without quantum number change are also allowed for magnetic dipole molecules. Millimeter-wave oxygen spectrum is influenced by the collisional coupling redistributing the absorption in comparison to the sum of the uncoupled line profiles [1].

Information on the O₂ microwave spectrum is of importance for applications. In particular, the band is used for retrieving vertical pressure and/or temperature profiles from remote sensing data. These applications require knowledge of the line parameters with high accuracy and models of the molecular oxygen spectrum in atmosphere, accounting for the coupling effect.

There is noticeable reciprocal influence between considered groups of the lines through the collisional process. Adjusting model parameters for the band shape changes calculated absorption in the wings of the band far from resonant lines. Current study considers "perturbative" approach [2] providing analytical band profile description used in MPM (Millimeter-wave Propagation Model) and one based on the semi-empirical collisional cross-sections calculations [3] within ECS (Energy Corrected Sud-den) formalism.

Earlier models [4,5] has shown inconsistency of the calculated absorption at the band wings. This led to the review of the resonator spectrometer recordings from the year of 2009 models were based on. The data were refined for oxygen concentration value reassignment for each recording. With the refined data, aforementioned models of the millimeter-wave oxygen spectrum in atmosphere were updated. Up-to-date broadening coefficients and their temperature dependences [6] were also included in the models. Updated models provide better residuals for the data they are based on, as well as better representation of the later independent measurements data (not used for models optimization) and better agreement between the models.

Line intensities, central frequencies and broadening coefficients included into models are known up to finite uncertainty, which leads to the uncertainty of the calculated absorption value. Parameters accounting for collisional coupling derived from measurements also have uncertainties because of measurements noise as well as individual line parameters uncertainties.

Model spectroscopic parameters are partially correlated, i.e. joint variation of the parameters values might not change the calculated absorption. Correlation of the parameters for both aforementioned models was estimated together with the calculated absorption uncertainty influenced by this correlation. This uncertainty can also be propagated to the brightness temperature calculation uncertainty.

The work was supported by RFBR grant 18-02-00705.

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Anharmonic IR spectra of chemical warfare agents from ab initio molecular dynamics simulations

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Chemical warfare agents (CWAs) are one of the most dangerous chemical compounds used against humans, mostly at war conditions but also in terrorist attacks. The most popular CWAs, for example sulfur mustard (HD), adamsite (DM) or Clark I (DA), are relatively small molecules with a limited number of degrees of freedom. Since these chemical compounds are extremely dangerous their research is restricted to the selected certified laboratories and therefore the knowledge about their spectroscopic properties, in particular FT-IR spectra, is limited.

The small size of CWA molecules make them an ideal target for the theoretical studies utilizing state-of-the-art methods, including ab initio molecular dynamics (AIMD). The advantage of in silico research is the precise description of physicochemical properties of CWAs without the risk of the direct exposure.

We investigate the structural properties of the selected CWA molecules in the gas phase by Car-Parrinello molecular dynamics simulations. We perform thorough conformation analysis of different configurations using density functional theory to analyze the behavior of the system at finite temperature. For each local minimum structure the harmonic IR spectrum is obtained during the vibrational analysis procedure. As the last step, the anharmonic dynamical finite temperature IR spectrum from the Fourier Transform of the dipole moment autocorrelation function is obtained to mimic the experimental IR spectrum.

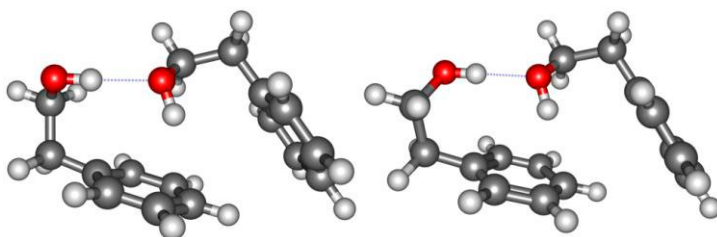
Observation of two dimers of phenyl ethyl alcohol using rotational spectroscopy

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Non-covalent interactions can be probed through the analysis of isolated neutral clusters in the gas phase. We examined the dimer and the monohydrate of phenyl ethyl alcohol as part of an on-going investigation on alcohol dimers using rotational spectroscopy. The adducts of phenyl ethanol were generated in a jet-cooled expansion and investigated by chirped-pulse Fourier transform microwave spectroscopy. Two conformers (C_i and C_s symmetry) were observed for the monomer, extending previous measurements to all monosubstituted ^{13}C isotopologues in natural abundance for the most stable species. Two isomers were observed for the dimer ($g-g+$ and $g+g+$), stabilized by a combination of $\text{OH}\cdots\text{O}$, $\text{OH}\cdots\pi$ and $\text{C-H}\cdots\pi$ interactions. Structural comparisons with the monohydrate illustrate the structural role of the aromatic ring in the dimer. Ab initio and DFT calculations will also be presented.



Self-aggregation process in CH₂F₂: large homoclusters studied by rotational spectroscopy

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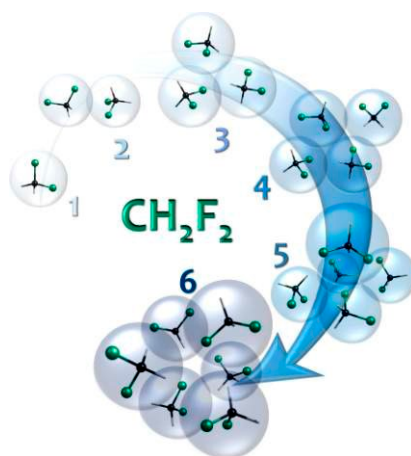
- 1) Physical Chemistry Department, Universidad del País Vasco (UPV/EHU), Bilbao, Spain. Biofisika Institute (CSIC, UPV/EHU), Universidad del País Vasco (UPV/EHU), Bilbao, Spain.
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The interest in halocarbons is still open. From an environmental point of view, the search for compounds alternative to freon is addressed to resolve the problem of the global warming; while from a strictly chemical point of view, non-covalent interactions that keep these molecules together are part of weak interactions, which behavior differ from the typical of strong ones (like H-bonds), enhancing their interest. Actually, the weak interactions characterizing the aggregation of these systems allow testing both the computational and the experimental fields, since predicting and measuring clusters held together by small binding energies is even today a challenge. For these reasons, the study of the structural arrangements of large clusters of halocarbons can still be considered an interesting topic.

In this work, the structure of large clusters of difluoromethane (CH₂F₂) is presented combining state-of-the-art rotational spectroscopy and quantum chemical calculations. The development in the last years of chirp pulsed Fourier transform microwave (CP-FTMW) spectrometers intensified the studies of oligomers of relatively large asymmetric rotors, opening to the observation of greater molecular cluster difficult to detect.[1] This extensive study is a collaboration between different laboratories both for the measurements (CP-FTMW spectrometers of Bilbao (ES) and Virginia (USA)) and for the theoretical part (USA).

In particular, the challenging assignments of one pentamer, two hexamers, and one heptamer homoclusters of CH₂F₂ were carried out, highlighting the high sensitivity of the technique. The ability to create a dense network of different weak interactions is the main driving force for the stabilization of each system. These kinds of studies of relatively large molecular aggregates can be considered a bridge between microsystems and molecular bulk.[2,3] In this regard, the results obtained for CH₂F₂ heteroclusters with water molecules will be also mentioned.

Despite a considerable gap remains between cluster and bulk properties, the last advances of rotational spectroscopy opening to the identification of larger clusters in an isolated environment, represent a step toward detailed structural understanding of first stage of nucleation and aggregation processes.



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The nitrogen–nitrogen noncovalent interaction in the gas phase

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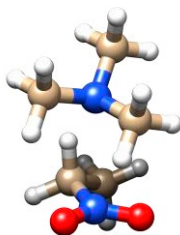
The N–N noncovalent interaction, along with weak C–H...O and secondary C–H...N hydrogen bonds, has been characterized in the gas-phase in the 1:1 nitroethane–trimethylamine complex by using state-of-the-art quantum-chemical computations combined with pulsed-jet Fourier-transform microwave spectroscopy.

The conformational potential energy surface has been deeply investigated by means of quantum chemical calculations rooted in density functional theory. In particular, three different minima and the corresponding connecting transition states have been identified. As for minima, rotational spectroscopic parameters, including rotational and centrifugal distortion constants as well as nitrogen nuclear quadrupole coupling constants, have been worked out by also accounting for vibrational effects by means of the generalized vibrational perturbation machinery [1] implemented in the Gaussian quantum chemical package [2]. The two most stable conformers are energetically nearly equivalent, and they present very similar structures and hence rotational parameters.

Experimentally, rotational transitions belonging to two different isopologues, namely the main isotopic species and that containing ¹⁵N–trimethylamine, have been measured and fitted by using the VMS–ROT module [3] of the virtual multifrequency spectrometer [4,5].

The nature and weight of the different contributions to the interaction in terms of charge rearrangement have been probed and quantitatively described by means of the “Natural Orbitals for Chemical Valence/Charge–Displacement” (NOCV/CD) scheme [6].

Given the small energy difference between the two lowest-lying minima (about 0.2 kcal/mol) combined with the low energy transition state (about 0.3 kcal/mol) ruling their interconversion as well as their almost equivalent rotational behaviour, the observed spectrum is consistent with either that of the global minimum or that of a structure continuously interconverting between the nearly equivalent conformers.



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Understanding structural similarities in the Homodimers of Fluorene, Dibenzofuran and Diphenylether via broadband rotational spectroscopy

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- 2) Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Leioa, Spain and Ikerbasque, Basque Foundation for Science, Bilbao, Spain
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- 5) Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany and Christian-Albrechts-Universität zu Kiel, Kiel, Germany

B7.4.

The role of inter and intramolecular interactions, such as hydrogen bonding and dispersion interactions, in stabilizing biological molecules is of great interest to many scientific communities. A detailed understanding of these interactions can be used as a design principle for stabilizing unusual molecules and molecular architectures. Therefore, a quantitative understanding of the various types of intermolecular interactions and their impact on the preferred molecular structure is an interesting topic.

In our group, we investigate these interactions using the high-resolution chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer COMPACT under the isolated conditions of a molecular jet in the gas phase. This technique provides accurate molecular parameters for developing a broad understanding of the underlying processes at the molecular level. To understand these weak interactions, we report here our studies on the homodimers of fluorene ($C_{13}H_{10}$), dibenzofuran ($(C_6H_4)_2O$), and diphenylether ($(C_6H_5)_2O$) using rotational spectroscopy in the region of 2–8 GHz. While their structures show overall similarities, they also have some differences: Fluorene is a polycyclic aromatic hydrocarbon that does not contain a polar group (Figure 1). Dibenzofuran replaces one CH_2 group in fluorene with oxygen, thus making it polar. In diphenylether, the C–C bond connecting the two rings in fluorene is absent, therefore, increasing the flexibility of the molecule. We will present the results of our systematic structural study of the series highlighting the differences and similarities in the observed homodimers.

Figure 1



Investigation of the products of thermal self-polymerization of Methyl methacrylate by means of microwave spectroscopy – the rotational spectrum of the dimer

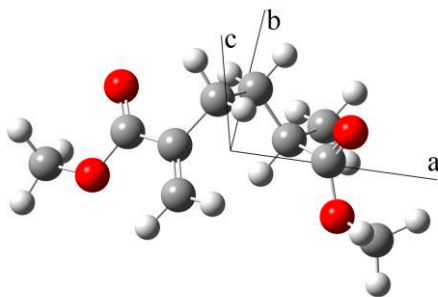
Sven Herbers¹, Daniel Obenchain¹, Peter Kraus¹, Kevin Lengsfeld¹, Henning Kuper¹, Jörg Becker¹, Jens-Uwe Grabow¹

1) Leibniz Universität Hannover

After the previous analysis of the monomer ($C_5H_8O_2$) of methyl methacrylate (MMA) by molecular beam Fourier transform microwave spectroscopy, this study is about the investigation of the dimer ($C_{10}H_{16}O_4$, figure below) of thermal self-polymerization. Segments of the spectrum from 3.3 to 21.2 GHz were recorded using the narrow band Fabry-Perot

resonator based COBRA-FTMW-spectrometer. 1508 molecular transitions were identified, of which 545 were assigned to a conformer of the dimer. Using the XIAM fitting program, rotation constants, Watson's S centrifugal distortion coefficients, and internal rotation parameters were obtained from the spectrum. The dimer contains three methyl rotors but only the two methoxy rotors cause resolvable (> 5 kHz) splittings of the rotational transition lines. The experimental results are compared with the results of ab initio calculations to find a suitable prediction method for the methyl methacrylate system.

The methyl methacrylate self-polymerization system is intended as an easy to access model system for polymerization processes and the analysis of the dimer presented in this study contributes to the stepwise understanding of the system by microwave spectroscopy and ab initio methods.



Application of molecular spectroscopic databases for certification of calibration gas mixtures

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Available molecular spectroscopic databases and catalogues were created without the involvement of the metrological community. This is the reason why modern spectral optical methods are not fully implemented in gas analysis. However, it is possible to use the available spectroscopic databases for high-precision measurements. In this paper, we present our approach to measuring the concentrations of gas components (HCl, CO, NO, SO₂) in gas mixtures using the HITRAN or GEISA molecular spectroscopic databases. Metrological traceability is usually implemented through the comparison of gas mixtures with high precision (comparison standards (CS)) made with the use of the National Primary Measurement Standard of Mole Fraction and Mass Concentration of Components in Gas Media (GET 154–2016) and working standards used to calibrate gas analyzers.

Methods of UV absorption[1], FTIR[2], and CRD[3] spectroscopy were developed and investigated to transfer units of mole fraction of gases to the working gas standards, to reduce the required number of CS and improve the accuracy of measurements.

The calculated spectra differ from the measured spectra taken for the same concentration of gas due to the inaccuracy of the absorption cross-section or inaccuracy of the spectral line parameters, presented in the molecular spectroscopic databases and catalogues. This is the reason why modern spectral optical methods are not fully implemented in gas analysis.

Also, for any spectral instrument, it is necessary to have a precise knowledge of the instrument function and the other technical parameters. Only one special gas cell is used to control the instrument function.

For the successful application of the existing molecular spectroscopic databases in the absorption spectroscopy, it was necessary to identify the most accurate data and attribute uncertainty to it, based on our own experimental studies conducted with the use of the metrologically assured CS. In the future, the measurement of concentrations can be done without the use of the CS.

In the case of CRD spectroscopy, for the gas mixtures in which the matrix gas differs from the air, the broadening of spectral lines associated with interactions between molecules leads to significant inaccuracy of measurement[3].

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Comb-calibrated coherent Raman spectroscopy of molecular hydrogen

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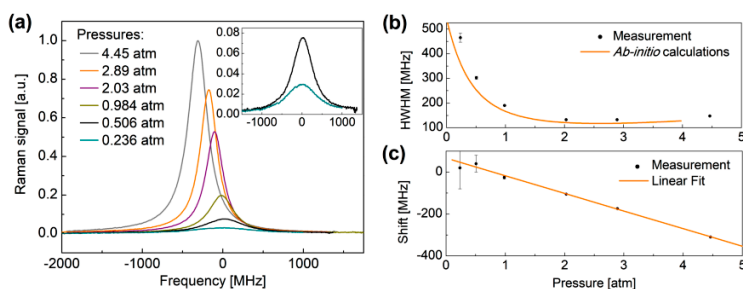
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Highly accurate measurements of H₂ transition frequencies is fundamental for testing the quantum electrodynamics and physics beyond the standard model [1–3]. However, the retrieval of the unperturbed line positions is very challenging since it compels to work in low pressure conditions: the achievement of high signal-to-noise ratios is then hindered by the weakness of quadrupole transition moments and by the low molecular density. Alternatively, the distortion of the line profile at higher pressure could be carefully modelled in order to compensate for speed-dependent collisional effects and for the strong Dicke narrowing. High accuracy measurements of the Q(1) transition of the pure H₂ 1–0 band at 4155.25 cm⁻¹ have been performed from 0.2 to 5 atmosphere using stimulated Raman spectroscopy. An Er:fiber frequency comb has been used to calibrate the frequency difference between the pump and Stokes cw lasers involved in the Raman process. The pump laser emits at 737.8 nm and is kept fixed while the Stokes laser is scanned over 3 GHz around 1064 nm. The two beams are spatially superimposed and travel through a multipass cell filled with H₂. Figure 1 (a) displays the line profiles measured at seven different pressures (the measurements at the two lowest pressures are displayed in the inset). As it can be noticed from panel (b) the retrieved widths are in a good agreement with ab-initio values based on H₂–H₂ quantum scattering calculations. The frequency shift, plotted in panel (c), is proportional to pressure above 1 atm and the retrieved pressure coefficient agrees well with previous results [4]. The strength of the approach which provides high signal-to-noise ratio and frequency accuracy at the same time enables the use of more advanced profile models, such as the Hartmann–Tran profile, for line shape investigation.



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[3] J. Mol. Spectrosc. 2014, 300, 55

[4] J. Quant. Spectrosc. Radiat. Transf. 2016, 177, 75.

Design and fabrication of a high-resolution Fourier-transform spectrometer with a supercontinuum laser source

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The perfect instrument in spectroscopy consists of a broadband instrument that measures spectra with high resolution and high sensitivity in a small amount of time. Fourier transform spectrometers allow for both high resolution and broadband measurements thanks to their multiplex advantage [1]. By coupling an optical cavity to a coherent light source, the sensitivity of the instrument, that is the ability to measure small concentrations, is considerably improved because the interaction length of the light with the sample is increased by several orders of magnitude [2].

The poster presents the first results regarding the design and fabrication of a homemade instrument that will embody all these features. This spectrometer is designed for the analysis of molecules and molecular complexes in the gaseous phase from the near infrared to the UV ranges with a resolution down to 0.0035 cm^{-1} . The homemade Fourier transform spectrometer has the particularity to employ a supercontinuum laser as the broadband light source.

Several measurements were performed to validate the experimental setup. Those are direct absorption spectra of the hyperfine transitions in Rubidium around 780 nm, of forbidden electronic transitions $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ in O_2 around 766 nm, and absorption of H_2O and CO_2 between 1.3 and 1.6 μm .

C7.3.

[1] P. R. Griffiths, Fourier transform infrared spectrometry (2007) (Vol. 171).

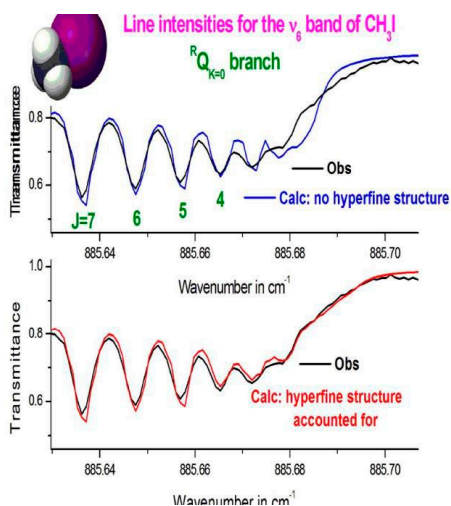
[2] F. Adler, et. al., Annu. Rev. Anal. Chem., (2010). 3, 175.

Line intensities for the ν_6 and $2\nu_3$ bands of Methyl Iodide ($^{12}\text{CH}_3\text{I}$)

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- 5) Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539, Ecole Polytechnique, Université Paris-Saclay, RD36, 91128 PALAISEAU Cedex, France.

The goal of this study is to measure for the first time absolute line intensities for the ν_6 band of methyl iodide (CH_3I) centered at 892.918 cm^{-1} . High-resolution Fourier transform spectra were recorded for the whole $500\text{--}1450\text{ cm}^{-1}$ spectral range at various pathlength-pressure products. Using these spectra, a large set of CH_3I individual line intensities was measured for the ν_6 band and least squares fit to derive the expansion of the ν_6 transition moment operator. For both line positions and intensities, the theoretical model accounts for the hyperfine structure in the 6^1 and ground states and for the vibration-rotation resonances that couple the 6^1 energy levels with those of the 3^2 and 2^1 vibrational states [A. Perrin *et al.*, *J. Mol. Spectrosc.* 324 (2016) 28 – 35]. As the $2\nu_3$ band is extremely weak, its associated transition moment operator was estimated from band strength collected in the literature. A comprehensive list of line positions and intensities was generated at $10\text{ }\mu\text{m}$ for the ν_6 and $2\nu_3$ bands of CH_3I .



Automatic assignment and fitting of spectra with PGOPHER

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2) *Canadian Light Source, University of Saskatchewan, Canada*

This poster describes the latest version of the pgopher program [1] (<http://pgopher.chm.bris.ac.uk>), which includes two new tools for computer assisted assignment of spectra. The first tool tries many different assignments, and a preliminary version of this has already been presented [2]. The second tool, a nearest lines plot, provides a clear indication as to whether a trial calculation is plausible, and gives good results even for dense spectra with no obvious structure and in the presence of interfering absorptions and/or perturbations. The effectiveness of these tools is demonstrated by the analysis of high resolution IR spectra of several bands of *cis*- and *trans*-1,2-dichloroethene, including hot bands and isotopologues in many cases. For these spectra, the tools working together allow up to 10,000 lines to be rapidly assigned for each band.

C7.5.

[1] C. M. Western, JQSRT, 2016 186, 221.

[2] C. M. Western and B. E. Billinhurst, PCCP, 2017, 19, 10222.

Does one need a high resolution in matrix isolation studies? The symmetry changes of the $^{28}\text{SiH}_4$ molecule in low-temperature matrixes

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Konstantin G. Tokhadze¹

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A8:1.

Today more and more researchers understand that low temperature inert matrices are not so inert. Beside the influence of matrix as media, the shift, for an example, of the frequencies of the bands in compare with the gas phase, there are many examples of so-call matrix effects. They say about sites or matrix splitting to describe some spectra features. It is connecting often with different deformation of molecules in matrices. The high symmetry molecules can be very good indicators of such deformations, since the changing of symmetry results qualitative changes in the spectra. If the band splittings are well-defined, the accurate characterization of the interaction between the molecule and the matrix environment can be performed, and the value of these splittings can serve as a benchmark for testing of the models describing such an interaction.

We present recent results [1] on $^{28}\text{SiH}_4$ in nitrogen and argon matrices in the temperature range of 7 – 20 K obtained by high resolution vibrational spectroscopy. The IR absorption spectra were recorded with a Bruker IFS 125HR Fourier spectrometer with a resolution of 0.1 – 0.01 cm^{-1} in the regions of fundamental and combinational bands. The frequencies and especially the values of splittings of the bands were determined. Additionally we paid attention to the relative intensities of split components. The study confirms the previous conclusions [2,3] that the symmetry of SiH_4 molecules changes from T_d to C_{3v} upon transition from the gas phase to the nitrogen matrix. The analysis of the spectra obtained in the argon matrix shows that under such conditions, there are at least two types of SiH_4 with symmetry of D_{2d} and C_1 . The interaction of argon matrix with a SiH_4 molecule is weak and the splitting of the band in region of ν_3 stretching band is only 0.1 cm^{-1} . However, this splitting is larger than the width of the bands and can be registered in the high resolution spectra.

Acknowledgment. The study was supported by Russian Foundation for Basic Research [grant number 18-03-00520]. The spectra were recorded in the resource center 'Geomodel' of Saint Petersburg University.

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Gas to solid phase transition of theobromine: crystal vs amorphous structures

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A8.2.

Theobromine belongs to the xanthine alkaloid class of compounds, which include, among others, caffeine and theophylline. It is a natural product present in high amounts in cocoa. Some studies suggest that theobromine inhibits the nucleation process and crystal growth of uric acid in the human body, [1] but specific information regarding the first stages of its nucleation are still unknown. In this work, we deal with the first stages of the aggregation of theobromine to form molecular clusters, and with the interactions that govern this process.[2]

Using laser vaporization and subsequent fast cooling by supersonic expansion, we generated solid clusters containing up to four theobromine molecules. Comparison of the IR spectrum of these aggregates with the predictions obtained using computational chemistry, we were able to characterize their structure and to unravel the amorphous nucleation pathways that the aggregation process follows. Such results were correlated with the two-, three- and four-body interactions found in theobromine crystals, obtained by a slow cooling deposition process.[3] The direct comparison of this gas-to-solid phase transition obtained using different conditions (see Figure 1), allows us to build a global picture of the nucleation of theobromine.

This deep analysis of theobromine led us to conclude that formation of the crystal by slow cooling and production of the amorphous solid in the supersonic expansion exhibit similar steps, up to a point at which, they take two different pathways.

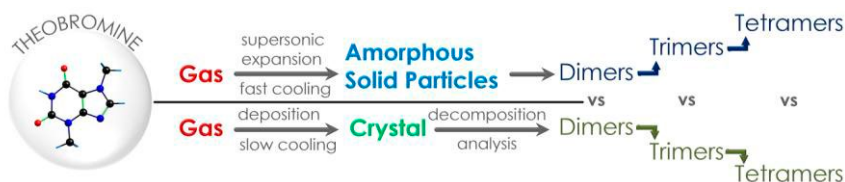


Figure 1. The structure of Theobromine and the scheme of the analysis.

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Seeing more does not necessarily mean seeing clearly

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A8.3

Organic dye aggregation in aqueous solution has been addressed in many experimental studies. Generally, an aromatic stacking interaction is thought to be the cause of the aggregation. One starts with the monomer–dimer equilibrium and expects larger aggregates upon increasing dye concentration in solution. This scenario is logical when one deals with neutral species. In contrast, for charged species the Coulomb repulsion should prevent stacking. In such molecular systems, the enthalpic part of the free energy is mainly controlled by anion–cation interactions. Thus, the latter interactions cannot be excluded from the discussion.

Let us consider acridine orange (AO) as the most studied example. In basic aqueous solutions at pH > 11 the absorption of AO is centered at 430–435 nm. The absorption wavelength decreases down to 417 nm in n-heptane. In both cases one deals with a monomeric AO. We are not aware of any dependence of the absorption on the concentration of the monomeric AO in solution. In neutral and acidic aqueous solutions at pH < 10 AO becomes protonated. The corresponding absorption spectra exhibit up to three bands centered at 490, 467, and around 450 nm. The relative intensities of these bands depend on dye concentration. It has been suggested that these bands belong to a monomeric cation (AOH)⁺, a doubly-charged dimer, and more complex aggregates, respectively. The bands at 490 and 467 nm have been observed in non-aqueous solutions of (AOH)⁺ as well. The fact that such aggregates are highly charged is ignored. Of course, one can somewhat reduce the enthalpic part of the free energy by assuming that the aggregation is anion-assisted, as it happens in crystals. However, it will be done at the expense of the entropic part.

On the other hand, the structure of acid–base complexes involving heterocyclic bases have been studied in details by NMR spectroscopy. One knows how the structural patterns depend on the acidity and the structure of the proton donor, solvent properties, and temperature. This knowledge can help us to elucidate the structure of the AO-aggregates at high concentrations and improve our understanding of intermolecular interactions in solution.

Titania- and montmorillonite- photocatalyzed synthesis of methane from carbon dioxide and the subsequent formation of nucleobases on early Mars and Earth

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Photocatalytic reduction of carbon dioxide on montmorillonite and TiO₂ can explain the formation of reduced gases in neutral atmospheres. CH₄ and CO were produced during 365 nm UV irradiation of CO₂ in the presence of HCl[1]. This photocatalytic reaction represents a simulation of the Martian atmosphere. Rate constants, external quantum efficiencies and effectiveness of the reduction process are discussed and compared to those estimated on Mars. Further, subsequent reprocessing of the CO + CH₄ and N₂ containing atmosphere (with the corresponding photocatalyst still present) was exposed to shock waves induced by a high-power laser. This simulated a high energy density event (e.g. an asteroid impact) on the surface of an early planet exposed to heavy bombardment by interplanetary matter. In the resulting mixtures, glycine and RNA canonical nucleobases were found[2]. Therefore, this process provides an explanation for the creation of reduced gases, the subsequent formation of simple biomolecules from neutral CO₂ rich atmospheres and also for the origin of CH₄ on Mars. The aim of this work was not to ultimately proclaim that the Earth's early atmosphere was globally reducing. Instead, evidence is presented to support the fact that the conversion of a CO₂ atmosphere to an atmosphere containing CH₄ and CO is possible. This conversion must be considered in models of initial early atmosphere transformations[3]. Therefore, a complete pathway leading from a neutral atmosphere to the formation of nucleobases under early Earth conditions has been demonstrated. Additionally, for the first time, this pathway is discussed in relation to the conditions of Mars upon solar irradiation and upon exposure to shock waves generated by the impacts of asteroids or comets. This work is a part of a research series funded by the Czech Science Foundation (grant no. 17-05076S, 13-07724S) and by Czech Ministry of Education, Youth and Sports for EU grant No. CZ.02.1.01/0.0/0.0/16_019/0000778. Part of this work was also financed by project GAUK 16742.

A8.4.

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Wavelength-meter controlled cavity ring-down spectroscopy for measurement of trace water vapor at ppt levels

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B8:1.

We developed a relatively simple technique to efficiently couple a laser frequency to a resonance frequency of a high-finesse cavity used in cavity ring-down spectroscopy (CRDS). The resonance frequency of the high-finesse cavity is stabilized with reference to the frequency of a helium-neon (He-Ne) laser. In this condition, the probe laser can easily be coupled to the cavity by controlling its frequency using a high-resolution wavelength meter, even using an inexpensive probe laser having a relatively broad spectral line width, such as a distributed-feedback (DFB) diode laser.

The method used to stabilize the resonance frequency of the cavity is essentially the same as that has been referred to as "frequency-stabilized (FS) CRDS [1]," but the technique to couple the laser with the cavity proposed in this study ("wavelength-meter controlled" technique) is relatively simple compared with those used in other studies on FS-CRDS.

The purpose of this study was to develop a CRDS-based trace-moisture analyzer capable of measuring trace water vapor (trace moisture) in N₂ even at ppt levels using the wavelength-meter controlled technique [2].

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CRDS of the collision induced absorption (CIA) band of O₂ at 1.27 μm

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In our atmosphere, the $a^1\Delta_g - X^3\Sigma^-g$ ($v=0-0$) absorption band of oxygen near 1.27 μm is formed by the superposition of local absorption lines with a broad absorption feature due to short-lived collisional O₂-O₂ and O₂-N₂ complexes, namely the collision induced absorption (CIA). The local lines corresponding to magnetic dipole transitions (and very weak electric quadrupole transitions) are of importance for air mass determination in several programs like the ground-based Total Carbon Column Observing Network (TCCON) and the CNES satellite MicroCarb.

In the present work, the CIA coefficients of the oxygen band at 1.27 μm are measured by cavity ring down spectroscopy (CRDS) at room temperature. Twelve distributed feed-back laser diodes were used below 7920 cm⁻¹ together with an external cavity diode laser above this wavenumber. The $B_{O_2-O_2}$, $B_{O_2-N_2}$ and B_{O_2-Air} binary absorption coefficients are determined with a reduced uncertainty from series of low density spectra (from 0.36 to 0.85 amagat) of pure oxygen and N₂+O₂ mixture with O₂= 20.95%. The CIA was obtained by difference between the absorbing samples spectra and argon spectra recorded *for the same densities* after removal of the local contribution of the absorption lines. The achieved accuracy of the retrieved CIA relies on the high base line stability of the spectra (at the 2×10⁻¹⁰ cm⁻¹ level). In addition, the adopted sub-atmospheric pressure values have the advantage to minimize the uncertainty related to the subtraction of the local lines. Although more accurate, our CIA coefficients show a good agreement with previous high pressure FTS values by Maté et al. [1] recommended by the HITRAN2016 database. For instance, deviations limited to a few % are noted for the B_{O_2-Air} coefficient.

B8.2.

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Cavity-enhanced dispersion spectroscopy for the highest accuracy applications

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We demonstrate comparison between absorption and dispersion spectroscopy in the optical cavity to estimate applicability of both approaches to the highest-accuracy applications. In many cases of reference spectra, e.g. for atmospheric applications, high dynamic range of absorption is crucial. Such conditions often lead to not negligible systematic errors of retrieved line parameters, exceeding the noise level and in consequence sub-percent uncertainties of line intensities and line shape parameters are not achievable. In the case of widely used cavity ring-down spectroscopy (CRDS) its dynamic range is limited by a bandwidth of detection system.

In this study we compare accuracy and dynamic range of CRDS, cavity mode width spectroscopy (CMWS) [1] and cavity mode-dispersion spectroscopy (CMDS) [2]. The frequency axis is linked through the optical frequency comb to the primary frequency standard [3]. Comparison is done on spectra of a weak ro-vibrational line from (3-0) band of CO, measured simultaneously with all three methods and fitted with the Hartmann-Tran profile (HTP) [4,5] and multi-spectrum fitting technique [6,7]. We prove predictions from our earlier paper [2] that contrary to both absorption methods CMDS spectrum has no indication of any systematic errors at sub-per-mille level of line intensity, even at high-opacity conditions and signal-to-noise ratio above 10^4 . This immunity to systematic errors results directly from replacing the intensity by the frequency measurements.

Our results suggest a paradigm shift from absorption to dispersion spectroscopy in the most demanding applications, e.g. reference data for atmospheric studies and testing ab initio line parameters, Doppler thermometry, isotope ratio measurements and basic research related to testing the Standard Model. CMDS can also be implemented into high-resolution and broadband direct optical frequency combs spectroscopy [8,9].

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H₂-He scattering states observation with cavity ring-down spectroscopy

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B8.4.

We present observations of scattering states of H₂ perturbed by helium. We set together *ab initio* lineshape parameters calculated based on the H₂-He interaction potentials [1] with highly accurate cavity-enhanced spectroscopic data using well physically justified line-shape profile – the Speed Dependent Billiard Ball profile (SDBBP) [2–3].

The system of hydrogen molecule in its ground electronic state perturbed by helium consists of only four electrons. It is a fundamental molecular system perturbed by an atom. The performed *ab initio* calculations of H₂-He interaction potentials allowed us to derive line-shape parameters from first principles [1]. We compare the entirely *ab initio* SDBB profile with highly accurate experimental molecular transitions of H₂. The achieved agreement between the *ab initio* and experimental spectra is at the level of 1%. Within this approach not only the shapes of experimental lines are reliably reproduced, but also the underlying physics of molecular collisions can be traced. Besides the analysis of the basic line-shape effects (such as relaxation or phase changes of the internal states of the molecule), we also analyse the more sophisticated ones such as speed-dependent effects or velocity changing collisions (complex Dicke narrowing parameter) [3–4], which are particularly pronounced for the H₂/D₂-He systems [1,5–7].

According to our knowledge, this is the first comparison of highly accurate experimental spectra with advanced *ab initio* models which includes the speed-dependent and velocity-changing collisions effects. It allows us to study quantum scattering for molecules as well as to validate *ab initio* quantum potentials in ranges very challenging for quantum chemistry methods (for instance, for highly stretched molecules).

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High resolution infrared laser jet-cooled spectroscopy of small van der Waals clusters with rare gases

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Weak intermolecular van der Waals (vdW) interactions play an essential role within large systems such as the bulk phase and macromolecules, because of the significant effect on structural and internal dynamics properties induced by many possible interactions. High resolution (HR) spectroscopy has proved to be a suitable method, primarily in the microwave and millimeter-wave regions to characterize finely the vibration-rotation-tunnelling (VRT) ground states of complexes with large amplitude motions and any other transitions due to the non-rigidity of the complex. More recently, the advent of HR infrared (IR) laser spectroscopy coupled to supersonic jets opened the way to a direct determination of the potential energy surface (PES) of linear triatomic molecules[1] interacting with rare gases (Rg) based on precise structural parameters derived from the fitting of spectra to provide ground and excited state rotational constants. Dynamic and structural data could be more challenging to extract in the case of floppy complexes with internal rotor or umbrella inversion motions, or with heavy rigid partners having small rovibrational constants.[2]

Taking advantage of an IR tunable laser spectrometer recently implemented at MONARIS, which combines a pulsed supersonic jet with a quantum cascade laser in the 10.5 μm region, two recent HR IR laser jet-cooled studies involving mixed vdW clusters will be presented: the first one about the $\text{NH}_3\text{-Ar}$ complex in the ν_2 umbrella region of NH_3 reports the measurement of five ortho and para bands unambiguously assigned on the grounds of rovibrational analysis for the ortho ones and by comparison with *ab initio* VRT levels from a four-dimensional PES surface for the para bands. The *ab initio* results turn out to be very predictive in terms of band centres, upper state rotational constants, tunnelling frequencies and relative weight of Coriolis couplings in the ground and excited ν_2 states.[3] The second one about small $\text{SF}_6\text{-Rg}$ ($\text{Rg} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$) clusters exploits the precise S-Rg bond lengths derived from the rovibrational analysis of jet-cooled laser spectra to evidence that vibrational band shifts measured with respect to the SF_6 monomer can be modeled by a radial Buckingham intermolecular potential containing both long-range attractive and short-range repulsive contributions. Also, signatures of larger clusters containing up to three Rg atoms are shown to be consistent with the additivity of vibrational shifts, in particular for Ar.[4]

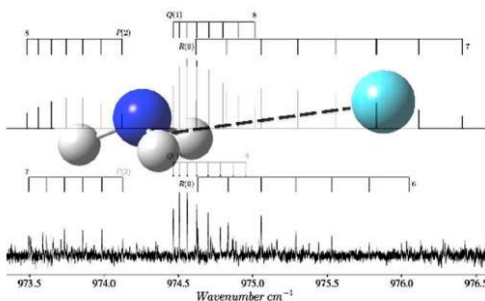


Fig. 1: Jet-cooled laser spectrum of the highest transition $\Pi_{\text{upper}}(l = 1, k = 1) \leftarrow \Sigma_{\text{lower}}(l = 1, k = 1)$ in *para*- $\text{NH}_3\text{-Ar}$ compared to the theoretical spectrum of the same transition at a rotational temperature of 3 K generated with our VRT levels and transition line strengths.

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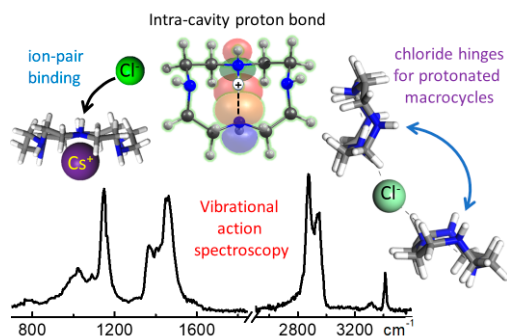
Insights into the binding of protons, cations and anions by azamacrocycles

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Supramolecular complexes formed by the N-substituted crown ethers cyclen and hexacyclen with protons, alkali and transition metal cations and halogen anions, are investigated with action vibrational spectroscopy, ion mobility, high resolution mass spectrometry and quantum-chemical computations. Several benchmark effects are addressed, such as intra- and intermolecular proton bridges, ditopic ion-pair binding, or the oligomerization of the macrocycles in linear arrangements mediated by halide hinges. Specific spectroscopic signatures of proton delocalization or proton-halide interactions are exposed, plausibly involving anharmonic behavior, which poses important challenges for the accurate molecular modelling of these systems.



Infrared spectroscopy and quantum-chemical calculations on diacetylene complexes: a joint experimental study and theoretical investigation on $\text{OCS-H}_2\text{C}_4$ and $\text{N}_2\text{O-H}_2\text{C}_4$ dimers

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In this contribution we present the results of a joint experimental study and theoretical investigation recently carried out on the weakly bound complexes of diacetylene, H_2C_4 , with OCS and N_2O . By using both a tunable diode laser and a QCL source coupled to a pulsed supersonic slit-jet expansion, the infrared spectra of $\text{OCS-H}_2\text{C}_4$ and $\text{N}_2\text{O-H}_2\text{C}_4$ were recorded around 4 mm, and the bands located in the region of the ν_1 fundamental band of OCS (about 2050 cm^{-1}) and N_2O (about 2200 cm^{-1}), respectively, were analyzed. These bands have hybrid rotational structure which allows for estimates of the orientation of OCS and N_2O in the plane of their respective dimers. From the rovibrational analysis both $\text{OCS-H}_2\text{C}_4$ and $\text{N}_2\text{O-H}_2\text{C}_4$ dimers were found to have planar structure with nearly parallel monomer units; analogous bands for $\text{OCS-D}_2\text{C}_4$ and $\text{N}_2\text{O-D}_2\text{C}_4$ were also measured and analyzed. Quantum-chemical calculations were carried out to identify the stationary points on the potential energy surface of both the dimers, and to characterize them in terms of structures and binding energies. From this analysis we identified four stable geometries for $\text{OCS-H}_2\text{C}_4$ and three for $\text{N}_2\text{O-H}_2\text{C}_4$; on the most stable structure of both $\text{OCS-H}_2\text{C}_4$ and $\text{N}_2\text{O-H}_2\text{C}_4$ dimers we performed additional calculations at coupled cluster level of theory to further refine their structural parameters. The predicted data, obtained by computations carried out at both $\text{CCSD(T*)-F12c/VTZ-F12}$ and CCSD(T)/CBS levels of theory, corrected by anharmonic effects computed at DFT level, were in very good agreement with those experimentally obtained from the rovibrational analysis of the infrared spectra.

Infrared spectra of the carbon monoxide – water dimer and larger clusters

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The CO–water dimer has been studied previously in the microwave [1] and millimeter-wave [2] regions. Infrared spectra have also been observed accompanying the CO [3] and H₂O ν_2 [4] and ν_3 [5] fundamental vibrations. We have now observed the $K = 1 - 0$ subbands for CO–H₂O and –D₂O in the CO region, thus determining A rotational constants for the excited ($\nu(\text{CO}) = 1$) state. These bands are the exact analogs of the $K = 1 - 0$ millimeter bands studied by Bumgarner et al. [2].

Further b -type $K = 1 - 0$ subbands are observed around 2200 (H₂O) and 2198 (D₂O) cm⁻¹ which we assign to the combination band involving the C–O stretch plus the intermolecular in-plane CO rocking mode. The observed bands do not give us direct values for the intermolecular mode frequencies since we do not (yet) know the excited state A -values. But it appears that this frequency must be higher than the value of 19 cm⁻¹ predicted for CO–H₂O by Rivera–Rivera et al. [4]. There is also an apparent anomaly in that the CO–H₂O and –D₂O subbands are closer together than might be expected.

Finally, two bands which must involve larger CO – water clusters are observed. For CO–D₂O, they can be rotationally assigned, but for CO–H₂O they are broadened ($\gg 0.02$ cm⁻¹) by predissociation. Neither band corresponds to the previously observed trimer, (CO)₂–H₂O [6]. The first band, near 2158 cm⁻¹, involves a planar or near-planar species which is probably the other possible trimer, CO–(D₂O)₂. The second band, near 2150 cm⁻¹, involves a non-planar species which may be another isomer of the (CO)₂–D₂O trimer, or possibly the CO–(D₂O)₃ tetramer.

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Effect of fluorine substitution on non-covalent interactions in molecular complexes of aromatic compounds

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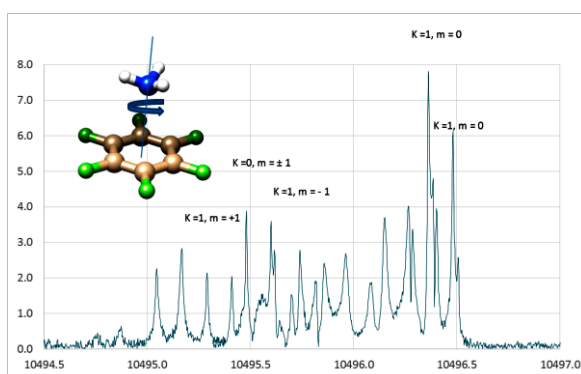
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The rotational spectra of pentafluoropyridine–water[1] and hexafluorobenzene–water[2] have shown unambiguously that substitution by fluorine atoms on the aromatic ring strongly influences its binding abilities causing both molecules to interact with water through a lone pair–p-hole interaction between the water oxygen and the ring.

A systematic study on the effects of fluorine substitution on the binding abilities of aromatic molecules was undertaken and we report rotational spectroscopy studies performed with a cavity based pulsed jet Fourier transform microwave spectrometer on a series of fluorine substituted pyridines, namely 2,4–fluoropyridine, 3,5–fluoropyridine and 2,4,6–fluoropyridine with water and more studies involving the complexes of pentafluoropyridine and hexafluorobenzene with different ligands such as NH_3 and CO .

In the complexes formed by the di-substituted pyridines, the water moiety forms an in-plane hydrogen bond with the heterocyclic nitrogen atom and this is by far the most stable conformation. In the tri-substituted pyridine–water complexes two isomers are possible, but the where the lone pair–p-hole form is present is the one observed in the rotational spectrum. The same interaction is present when pentafluoropyridine and hexafluorobenzene are used as substrate for the binding of CO and NH_3 .

From the spectroscopic constants of various isotopic species the structures and the parameters related to the observed large amplitude motions have been determined, while theoretical calculations have allowed the unveiling and quantification of the different interactions present in the complexes.



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Chalcogen bond formation: The non-covalent, intermolecular sulfur–sulfur interaction of dimethyl sulfide and sulfur dioxide

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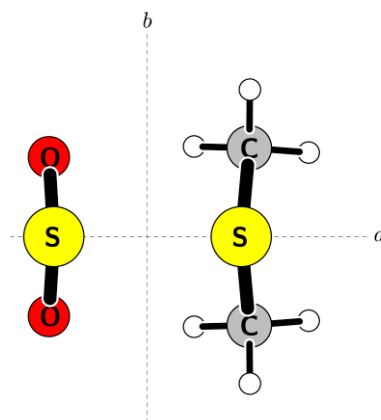
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An analog to the well-studied halogen–halogen bond, the chalcogen–chalcogen interaction occurs when one chalcogen atom acts as an electron donor to another chalcogen. This combined experimental and theoretical study presents a detailed analysis of the sulfur–sulfur interaction in the dimethyl sulfide and sulfur dioxide complex. The gas-phase chalcogen–chalcogen noncovalent interaction has been characterized by using state-of-the-art quantum-chemical computations combined with cavity type Fourier-transform microwave spectroscopy.

Rotational transitions belonging to seven different isotopologues, which are split by the motion of the two methyl tops of dimethyl sulfide, were fit using the XIAM program [1]. The abundance of isotopic information allows for a detailed determination of the structure of the complex. From the theoretical point of view, the accurate equilibrium structure was computed by exploiting the so-called “cheap” geometry scheme,[2] whose reliability also for molecular complexes has been demonstrated recently for the pyridine–ammonia complex [3]. From this, accurate equilibrium energetic and spectroscopic parameters have been computed, and corrected for zero-point energy and anharmonic vibrational effects obtained from density functional theory calculations.

The abundance of isotopic information allows for a detailed determination of the structure of the complex. Semi-experimental equilibrium and effective structures were determined using the Molecular Structure Refinement (MSR) software [4] taking into account anharmonic vibrational corrections at the B2PL-YP-D3/mau-cc-pVTZ-dH level [3]. The sulfur–sulfur interaction was further characterized by means of the nuclear quadrupole coupling in single ³³S substituted species of the complex and isolated molecules. The results of the “Natural Orbital for Chemical Valence/Charge-Displacement” (NOCV/CD) scheme [5] are also presented. Finally, chemical interaction energies were derived using the well-known pseudo-diatomic model [6] and compared with that were obtained theoretically from the “cheap” composite scheme.



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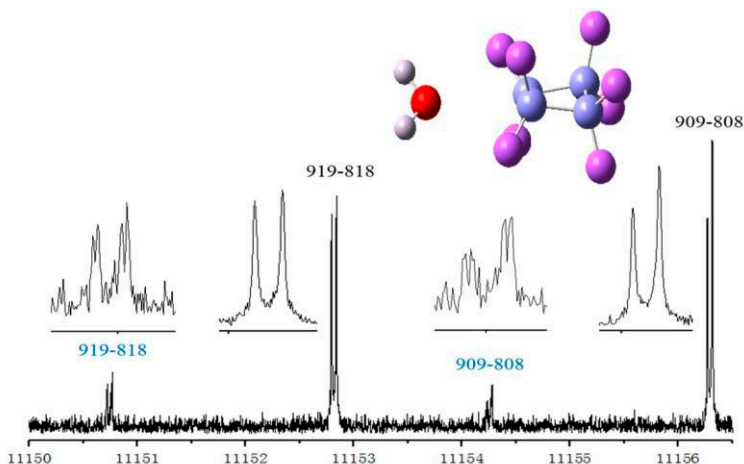
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Halogen bond and internal dynamics in Perfluorocyclobutane–water

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The rotational spectrum of the perfluorocyclobutane–water complex has been studied by Fourier transform microwave spectroscopy, which shows that the oxygen of water points toward the center of one of the C–C bond, forming a sort of halogen bond. Each rotational transition is split into three or four components, indicating that the internal rotation of water might be coupled with the ring puckering.



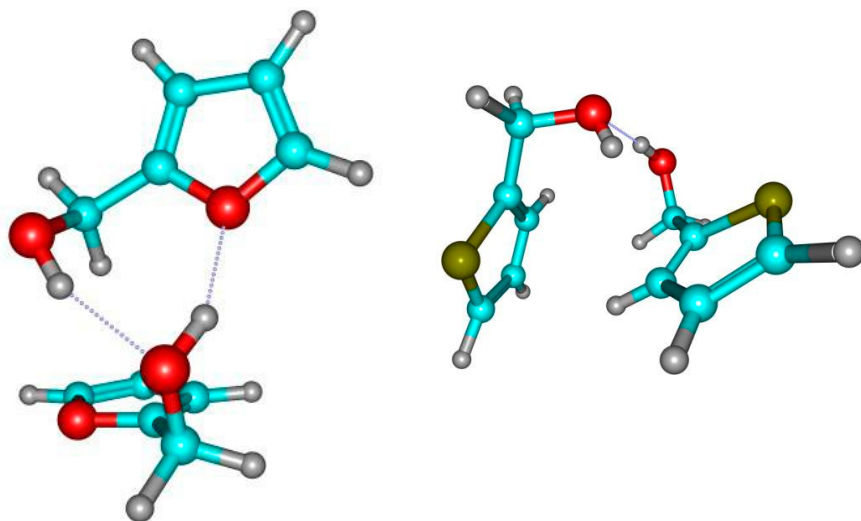
Rotational spectroscopy of the dimers and monohydrates of furfuryl alcohol and thenyl alcohol

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The dimers and the monohydrates of thenyl alcohol (TA₂, TA-H₂O) and furfuryl alcohol (FA₂, FA-H₂O) have been generated in a supersonic jet expansion and probed using both chirped-pulse and cavity Fourier transform microwave spectroscopy. The experimental results and supporting ab initio molecular orbital calculations allow comparing the conformational preferences and the role of the sulfur and oxygen atoms in the O-H...O/O-H...S/S-H...O hydrogen bonds (HBs) stabilizing the dimers. In the furfuryl monohydrates water behaves as a proton donor to the ring oxygen, in competence with a second HB to the alcohol or thiol side chain. Different behavior was observed when the ring oxygen is replaced by a sulfur atom in the thenyl monohydrates, as the water molecule is binding to the side chain and the *p* electronic cloud of the ring. Large-amplitude motions caused by water in both thenyl dimers are detected by tunneling splittings of the rotational transitions. Spectroscopic, structural and computational data will be reported.



Microwave spectroscopic characterization of the S...O/N chalcogen bond

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The intermolecular complexes formed between 2,2,4,4-Tetrafluoro-1,3-dithiethane ($C_2S_2F_4$) and water/ammonia were investigated by pulsed jet Fourier transform microwave spectroscopy and theoretical calculations. For these complexes, the most stable conformers predicted at MP2/6-311++G(d,p) level of theory were observed. Rotational assignments, ab initio calculations and quantum theory of atoms in molecules (QTAIM) analyses indicate that the observed complexes are stabilized through S...O or S...N Chalcogen Bond. The determination of the molecular structure, the tunneling splitting, and the bonding nature of S...O/N interaction will be discussed.

Spectroscopy of new Imine astrophysics target: Methylimino-acetonitrile ($\text{CH}_3\text{N}=\text{CHCN}$)

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There are to date about 200 molecules that have been detected in the interstellar medium or circumstellar shells. Among these molecules, several tens are the methylated derivatives of compounds previously detected.

For several years, we have been studying molecules belonging to the imine family. Following the detection of the dimer of HCN, the cynaoethanimine, its methylated derivative appears as a privileged fiber. This molecule is methylimino-acetonitrile: $\text{CH}_3\text{N}=\text{CHCN}$. There are two isomers E and Z, the most stable isomer is the E whose energy is 124.4 cm^{-1} (1.49 kJ/mol) lower than that of Z. There was no spectroscopic data allowing detection without ambiguity of this molecules in the interstellar medium. We recorded and analyzed spectra up to 660 GHz.

This compound is not stable in laboratory conditions, it was produced in-situ by pyrolysis and introduced in a 1m long pyrex cell in a flow mode.

With regard to the E isomer, this is also an interesting case on spectroscopic point of view. Even if the internal rotation barrier is quite high 714 cm^{-1} , some A-E doublets due to the methyl top internal torsion were observed. This is due to quite high ρ value: 0.274, just slightly smaller than the acetaldehyde value of 0.329.

The analysis is performed using the RAM36 code (Ilyushin, V.V. et al; J. Mol. Spectrosc., 259, 26, 2010). The spectroscopic results will be presented.

These results were supported by the Programme National PCMI of CNRS/INSU with INC/INP co-funded by CEA and CNES, the French National Research Agency ANR-13-BS05-0008 "IMOLABS"

Imidazole rotation spectrum investigation for astrophysical search

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Many of the around 200 known interstellar molecules have been proposed as precursors in various synthetic networks which would yield higher organics in primordial environments (e.g. Strecker synthesis and Michael addition [1]).

Besides simple and ubiquitous interstellar species (e.g., H₂O, NH₃, HCN, H₂CO, etc.), more complex compounds may have been crucial in building up the molecular complexity on early-stage planetary bodies.

In particular, organic ring compounds play a key role in terrestrial biochemistry and, most likely, they were also pivotal ingredients in Earth's prebiotic chemistry.

Apart from the noteworthy large fullerene structures, relatively few organic ring molecules have been unambiguously detected in the interstellar medium.

Among those detected are c-C₃H₂ (cyclopropenylidene), c-C₂H₄O (ethylene oxide), benzene (c-C₆H₆), and cyanobenzene (c-C₆H₅-CN).

The recent tentative detection of 2H-azirine (c-C₂H₃N) and aziridine (c-C₂H₅N) have also been reported [2,3].

Larger N-bearing heterocycles, such as purines, pyrimidines and quinoline structures, have been identified in meteoritic organic matter (e.g. [4]).

The five-membered ring imidazole c-C₃N₂H₄ is a substructure of fundamental biological molecules such as purines and the amino acid histidine.

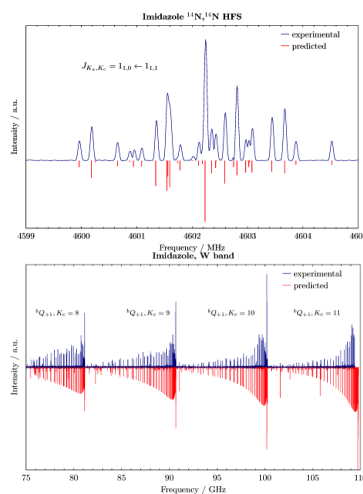
This species has been suggested as a possible candidate for detection in the interstellar medium due to its large dipole moment ($\mu_a \sim 3.7D$) and for its favourable partition function (no spin statistics).

An unsuccessful search in a sample of cold core clouds and massive star forming regions was performed almost 40 years ago [5].

During the last few decades, the performances of the millimeter telescopes have witnessed an impressive improvement in terms of sensitivity, spectral coverage, and resolution, considerably increasing the chance of new molecular detections.

Unfortunately, the only rotational studies of imidazole present in literature are limited to the cm-wave region [6,7], and the precision of the rest frequencies in the millimetre regime (the wavelength range best exploited by a state-of-the-art observing facility like ALMA) is not adequate.

Here we present a comprehensive investigation of the rotational spectrum of imidazole from 2 to 295 GHz. The 2–8 and 75–110 GHz frequency regions, were covered using the laboratory facility developed in the Schnell group at DESY (Hamburg). The spectrum in the 260–295 GHz region was taken in Pate's laboratory at the University of Virginia (Charlottesville).



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Laboratory rotational spectroscopy of isotopic species of Methyl Mercaptan, $\text{CH}_3^{34}\text{SH}$ and CH_3SD , and search for them in ISM

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Methyl mercaptan (also known as Methanethiol), CH_3SH , has been found in the warm and dense parts of high as well as low mass star-forming regions.^{1,2} Laboratory spectroscopy of its ^{34}S and D isotopologues and detecting them will enable astrophysicists to determine the $^{32}\text{S}/^{34}\text{S}$ as well as the respective H/D abundance ratios and relate those to the observed astrophysical environment. The molecule is also of fundamental interest because of the large amplitude internal rotation of the CH_3 group against its framework SH. The ^{34}S isotopic species of CH_3SH has been measured in natural abundance in the frequency ranges of 49–510 GHz and 1.1–1.5 THz.³ The spectrum of CH_3SD has been recorded in the range 150–510 GHz. The analysis of the spectra has been performed up to the second excited torsional state. For the ^{34}S isotopologue extensive assignments of $\Delta K = 0$ transitions in $v_t = 0$ to 2 have been done. Numerous assignments of $\Delta K = \pm 1$ transitions have been made in $v_t = 0$ and to a lesser extent in the two higher torsional states. The results of modeling these data with the RAM36 program and of searches for these isotopologues in our ALMA data of the 3 mm wavelength range will be presented.

Acknowledgments The work in Kharkov was done under support of the Volkswagen foundation. The assistance of Science and Technology Center in Ukraine is acknowledged (STCU partner project #P686). The work in Cologne was supported by the Deutsche Forschungsgemeinschaft (DFG) via grant SFB 956, project B3 and via the Gerätezentrum "Cologne Center for Terahertz Spectroscopy". LHX and RML acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada.

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Accurate millimetre and submillimetre rest frequencies for cis- and trans-dithioformic acid, HCSSH

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To better understand the sulphur chemistry of the Interstellar Medium (ISM), new S-bearing molecules must be studied in the laboratory, obtaining accurate rest frequencies for an astronomical search. Recently, many new S-bearing compounds have been detected for the first time in the ISM and chemical models have been improved through inclusion of these and other species, too. Notwithstanding this progress, some molecules are still not considered in the current picture of sulphur chemistry. We focus on the two isomers of dithioformic acid, trans- and cis-HCSSH, which is the sulphur analogue of formic acid.

We studied the species in the laboratory using the frequency modulation sub-millimetre absorption spectrometer at the Center for Astrochemical Studies (CAS) in Garching. The molecules were produced directly within a free-space cell by glow discharge of a gas mixture. We measured lines belonging to the electronic ground state up to 478 GHz, leading to a comprehensive centrifugal distortion analysis. Hence, the new dataset provided by this study can be used for astronomical search. In particular trans-HCSSH, the lowest-energy conformer, is the best candidate for a potential detection.

The nanocosmos gas Cell: A broadband Fourier transform millimeterwave spectrometer based on radio astronomy receivers

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B9.5.

A Gas Cell reactor for the study of the chemical composition and evolution in different astronomical environments has been built as a part of the NANOCOSMOS project. It employs the same detection system as those present in radio-telescopes, constituting a novel and state-of-the-art approach to do rotational spectroscopy with kHz resolution. In particular, it has been implemented with Q-band (31.5–50 GHz) and W-band (72–116 GHz) receivers analogous to those built for the 40 meters telescope of Yebes Observatory (CNTRAG-IGN, Spain). These receivers are sensitive to the rotational emission of the molecules present in a one meter Gas Cell (no external polarization needed). The technique provides large instantaneous bandwidth, spectral purity, and a linear dependence of the signals with the partial pressure. Some pictures of the instrument are presented in Figure 1. The full description of the previous prototype cell can be found in *I. Tanarro, et al. A&A 2018*. In the initial experiments of the Gas Cell as a rotational spectrometer, we recorded the spectrum of CH₃CN in the Q and W-bands. After an integration time of 11 minutes, we could observe its vibrational excited states up to ~1000 cm⁻¹ and its isotopologues in natural abundance, including ¹⁵N with a spectral resolution of ~38 kHz and an estimated detection limit of 10⁻⁶ mbar.

The Gas Cell is also equipped with a quadrupole mass spectrometer, a UV-Visible spectrometer, a cold plasma generator (inductively coupled RF discharge) and UV-lamps. All these components make of the Gas Cell a versatile instrument that allows a full characterization of gas mixtures directly introduced in the chamber and also of the reaction products formed in cold plasmas or by UV radiation of the mixtures. In the present communication, we report the results of our investigation about the UV and plasma effects on several gas mixtures that mimic different scenarios such as the interstellar medium, the stratosphere of Titan (CH₄, N₂), or the prebiotic terrestrial atmosphere (CH₄, NH₃, H₂O).

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC-SyG-2013 Grant Agreement No. 610256 NANOCOSMOS and from Spanish MINECO CSD2009-00038 (ASTROMOL) under the Consolider-Ingenio Program. We also thank Spanish MINECO for funding under grants AYA2012-32032, AYA2016-75066-C2-1-P, FIS2013-48087-C2-1-P, FIS2016-77726-C3-1-P, FIS2016-77578-R, MAT2014- 54231-C4-1-P and CONACYT in Mexico for grant 291842.



Figure 1: Pictures of Nanocosmos Gas Cell

Rotational spectroscopy signature of smelling allyl alcohols

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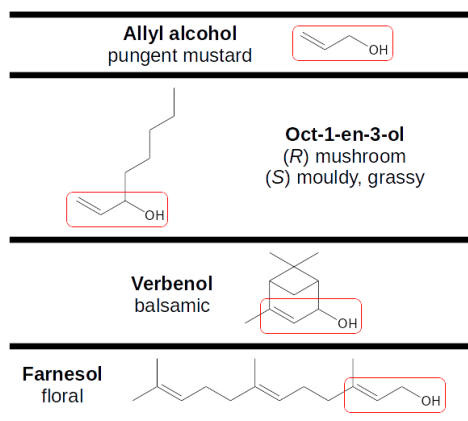
Allyl alcohol is a strong lachrymator with a pungent mustard odor. It is a fundamental building block of several smelling organic molecules. Depending on the carbon frame, they present a quite different odor, suggesting a modulation role of the molecular shape in the ligand–receptor interaction.

Rotational spectroscopy is a suitable tool to get insights on the structure of molecules and molecular complexes in the gas phase and, in combination with computational chemistry simulations, allows for exploration of high dimension conformational spaces. Here we present, for the first time, the rotational spectra and the analysis of three allyl alcohols: oct-1-en-3-ol (mushroom alcohol, C₁₀H₁₈O), 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol (verbenol, C₈H₁₆O), and 3,7,11-trimethyl-2,6,10-dodecatrien-1-ol (farnesol, C₁₅H₂₆O).

The spectrum of oct-1-en-3-ol has been collected in the 59.6–74.4 GHz frequency range with the free jet absorption millimeter wave spectrometer in Bologna. Two species were observed. In both of them the allyl alcohol substructure is *skew-gauche* (referring to OCC=C and HOCC dihedral angles, respectively) and the alkyl chain is all *trans*. The difference lies on the relative orientation of the alkyl and allyl alcohol subunits.

The spectrum of *cis*-verbenol has been recorded in the 2–8 GHz frequency range with the chirped-pulse Fourier transform spectrometer in Valladolid. The rotational spectra of the parent, hydroxyl deuterated, and all ¹³C-isotopologues have been assigned, allowing for structure's determination. Differently from solid state, in the gas phase the most stable conformer exhibits an *anti* HCOH arrangement. Observation of the 1:1 water complex has shown that water acts as proton donor to the hydroxyl group, forming a secondary O–H interaction with alkyl verbenol's hydrogen atoms.

With the same spectrometer, the spectrum of farnesol has been collected. Since farnesol is formed by a mixture of 4 *cis/trans*-isomers, the spectrum is quite congested and, due to the presence of 8 rotatable bonds, the assignment is not straightforward. Preliminary considerations on the conformational space will be presented.



DNA sugars: in the gas phase and in solution

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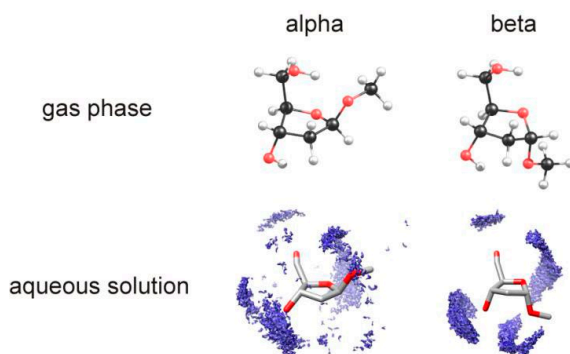
2) Department of Physical Chemistry, Universidad del País Vasco (UPV/EHU), Bilbao.

3) Department of Chemistry, Universidad de La Rioja, Logroño.

4) Chemistry Research Laboratory, University of Oxford, Oxford.

Sugars are versatile molecules that play a variety of roles in the organism. For example, they are important in energy storage processes or as structural scaffolds. Here, we focus on the monosaccharide present in DNA by addressing the conformational and puckering properties in the gas phase of α - and β -methyl-2-deoxy-ribofuranoside and α - and β -methyl-2-deoxy-ribofuranoside. Other sugars have been previously studied in the gas phase.[1,2]

The work presented here stems from a combination of chemical synthesis, supersonic expansions, quantum chemical calculations, microwave spectroscopy, NMR spectroscopy and Molecular Dynamics. Thanks to the alliance of these techniques, we have studied for the first time the conformational landscape of the sugar present in DNA in its biologically relevant form. Previous studies in the gas phase had been performed on 2-deoxyribose,[3] but only pyranose forms were detected. In this work, we isolate and characterize furanose forms of the sugar, which are the biologically active forms in DNA. Our gas phase study serves as a probe of the conformational preferences of these biomolecules under isolation conditions. Moreover, we compare the results obtained in the gas phase with data in solution thanks to a combination of NMR spectroscopy and Molecular Dynamics. In this way, we characterize the favored conformations in solution and, by comparing with the results under isolation conditions (gas phase), we extract the role of the solvent in the conformations and puckering of the monosaccharide.



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Multiresponsive Chromic Soft Materials: Formation of Macrocycles from Carbazole-based Biradicaloids

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π -conjugated biradical compounds become essential building blocks in DCC (dynamic covalent chemistry).[1] This field is based on the creation of structural scaffolds based on chemical components which interact through strong but reversible bonds. Importantly, dynamic covalent bonds will be at the center of attention because of their unique feature to become reversible under mild conditions.[2] Recently, we have demonstrated the reversible interconversion between a stable quinoid precursor based on a para-substituted carbazole with terminal dicyanomethylene groups and a macrocycle cyclophane upon soft external stimuli (temperature, pressure, light), which results on strong chromic features.[3] In this work, we investigate the interconversion of the monomer/cyclophane transformation in carbazole-based systems, both in solution and solid state, upon external stimuli. To this end, we use a combined experimental and theoretical study that links vibrational spectroscopy (Raman and IR) with DFT calculations.



Figure 1. Interconversion between 2,7-Dicyanomethylenecarbazole-based Biradicaloid (right) and Corresponding Cyclophane Tetramer (left).

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Raman spectroscopy as a versatile tool to study organic biradicals

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C9.4.

In recent years, there has been a renewed interest in the study of open-shell polycyclic aromatic hydrocarbons (PAHs). Among them, biradicals are characterized by a four states energetic model for the low lying electronic states. Such a distribution is related to the attractive electronic, magnetic and optical properties which make biradicals promising candidates for a wide range of applications in organic electronics, such as nonlinear optics, molecular spintronics, energy storage and organic photovoltaic devices sensitized by singlet fission. Despite all the promising properties predicted for open-shell PAHs, a common drawback still needs to be overcome: the high reactivity of radicals, which implies that most open-shell species tend to be too short-lived for practical applications and even for characterization [1]. In this regard, Raman spectroscopy has shown to be a suitable tool for studying this kind of molecular systems, able to provide valuable information that could be used in the development of new synthetic approaches [2].

Herein we report the study of different open shell PAHs with biradical character with the aim to highlight how Raman spectroscopy can help us to elucidate the molecular structure and the electronic configuration of their ground states and how the molecular information provided can be used to rationalize their properties in the context of the four states model [3–5].

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Molecular spectroscopic study on a natural uric acid type of Kidney Stone

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The studies on kidney stone at molecular level are essential for prevention of diseases. In this study, a natural uric acid type of kidney stones was collected in the Department of Urology, Medical Centre – University of Freiburg, Germany. Uric acid is a heterocyclic compound with the formula $C_5H_4N_4O_3$. Uric acid stones may exist as uric acid monohydrate $C_5H_4N_4O_3 \times H_2O$ and uric acid dihydrate $C_5H_4N_4O_3 \times 2H_2O$. FT-IR and FT-Raman spectra of the uric acid stone have been recorded to determine its vibrational properties and molecular constitutions, including the existing tautomers. Computationally obtained vibrational spectra of several tautomers of uric acid with B3LYP and PBE density functionals were compared with experimental results. This leads to unique assignment of experimental vibrational bands and to extract information about the existing tautomers.

M. Kocademir, A. Baykal, **M. Kumru**, M. L. Tahmaz, "Structural characterization and vibrational studies of human urinary stones from Istanbul, Turkey", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 160 (2016) 1–7

Keywords: Uric acid; Kidney stone; Vibrational spectroscopy

Poster presentations

In the following pages all posters abstract have been ordered by day.

The abstract numbers correspond to one of the two sessions in the scientific program in page 12. (Session 1: Tuesday; Session 2: Thursday).

You can search for specific authors in the author index at the end of this abstract book (all authors and co-authors are listed in alphabetical order with their abstract number/s).

DFT and TD DFT modeling of vibrational structures in high resolution MATI and REMPI spectra of chromium bisarene complexes

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Together with metallocenes, metal bisarene derivatives play key roles in both fundamental and applied organometallic chemistry because of their relevance for theoretical and experimental studies of metal–ligand bonding, organic synthesis, catalysis, metal-containing polymers, biomedicine and nanoelectronics. New insights into their electronic structures are provided by the high-resolution laser spectroscopic techniques exploring resonance enhanced and threshold ionization processes. The mass-analyzed threshold ionization (MATI) spectra of chromium bisarene complexes (C₆H₆–nRn)(C₆H₆–mRm)Cr (R = Me, Ph; n, m = 0–3) show complicated vibrational structures arising mainly from skeletal and CH modes. The DFT calculations of the Franck–Condon intensities at the B3P–W91/6–311++G(d,p) level of theory appear to reproduce very well the experimental high-resolution MATI spectra of the complexes with benzene, toluene, xylenes and biphenyl. The DFT modeling makes it possible to interpret the dependence of the MATI vibrational structures on the nature, number and location of the substituents in the rings. This is especially important for the sandwich systems bearing substituents in both ligands since these molecules form several rotational isomers [1, 2]. The new assignments of the MATI peaks to individual conformers are presented.

Another type of DFT modeling concerns vibronic structures of the REMPI spectra of bis(benzene) chromium and its deuterated derivatives. These structures correspond to the lowest Rydberg px,y transition. The R4px,y state is degenerate and the REMPI spectra reveal components arising from the Jahn–Teller active e2g vibrations [3]. To model the vibronic structures one needs to optimize the excited-state molecules and calculate the Rydberg vibrational frequencies. The latter task is extremely computationally expensive when using the TD DFT approach though the B3LYP/6–311++G(d,p) and BPW91/6–311++G(d,p) levels of theory provide a good agreement with the experiment. The much simpler variants of the REMPI simulations with use of the TD DFT Rydberg-state geometries and the Hessian obtained by stationary DFT with the ground-state neutral or cation wavefunction appear to give similar pictures. This can be explained by similarities in the bis(benzene)chromium Rydberg vibrational frequencies and those of ground-state (C₆H₆)₂Cr⁰ and (C₆H₆)₂Cr⁺ (both Rydberg transition and ionization involve the chromium non-bonding 3d_{z²} electron). The approaches developed in the present work will be employed for further prediction of the vibronic structures in high-resolution electronic spectra of other sandwich compounds.

Acknowledgements

This work was supported by the Russian Science Foundation (Project No. 18–13–00356).

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Vibronic emission spectroscopy of o-Ethynylbenzyl radical generated from corona discharge of o-Ethynyltoluene

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Whereas benzyl radical, a prototype of aromatic free radicals, had attracted much attention from spectroscopists for the subject of large molecular radicals,¹ alkyl-substituted benzyl radicals have been less studied, presumably due to the difficulties associated with production in corona discharge from precursors. Nevertheless, several alkyl-substituted benzyl radicals^{2,3} have been identified through the analysis of the vibronic emission spectra observed from the corona discharge of precursor molecules.

The o-ethynylbenzyl radical was generated from the corona discharge of precursor o-ethynyltoluene seeded in a large amount of carrier gas helium using a technique of corona excited supersonic expansion (CESE) coupled with a pinhole-type glass nozzle which has been well developed in this laboratory. The emission from the jet-cooled but vibronically excited radicals was recorded with a long-path monochromator in the visible region.

The vibronic spectrum observed was analyzed to determine the position of the origin band of the $D_1 \rightarrow D_0$ transition and identify the species generated in corona discharge by assigning the vibronic bands to the vibrational modes in the ground state.

The electronic transition of the o-ethynylbenzyl radical exhibits a large red-shift of the origin band with respect to the parental benzyl radical at $22,002\text{cm}^{-1}$, rationalizing the extension of π electron delocalization to ethynyl group which is conjugated to the benzene ring. The vibronic assignments of the bands clearly confirm the observation of the o-ethynylbenzyl radical in this experiment.

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High resolution study of CH₂=CD₂ molecule: line intensities and half-widths

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Present work is the next step in our study of high resolution spectra of the CH₂=CD₂ molecule [1–2]. Here we introduce the results of the line intensities and half-widths analysis in the region of 1400–1650 cm⁻¹.

The absorption spectra of CH₂=CD₂ in the region of 1400–1650 cm⁻¹ were recorded with a Bruker IFS 120HR FTIR spectrometer at the Technische Universität Braunschweig (Germany) under various conditions. Spectra assignment as well as the results of the ro-vibrational analysis were presented at HRMS-2017 [3].

Individual line strengths were determined from the fit of the line shapes using Hartmann–Tran profile. As to the line half-widths, a multi-spectrum fitting procedure with the Hartmann–Tran profile of lines was used, so self-broadening coefficients were obtained by fitting the measured line shapes recorded at various pressures.

P13.

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The classification of lung cancers and their degree of malignancy by FTIR, PCA-LDA analysis, and a physics-based computational model

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Lung cancer has the highest mortality rate of all malignant tumours. The current effects of cancer treatment, as well as its diagnostics, are unsatisfactory. Therefore it is very important to introduce modern diagnostic tools, which will allow for rapid classification of lung cancers and their degree of malignancy. For this purpose, the authors propose the use of Fourier Transform InfraRed (FTIR) spectroscopy combined with Principal Component Analysis-Linear Discriminant Analysis (PCA-LDA) and a physics-based computational model. The results obtained for lung cancer tissues, adenocarcinoma and squamous cell carcinoma FTIR spectra, show a shift in wavenumbers compared to control tissue FTIR spectra. Furthermore, in the FTIR spectra of adenocarcinoma there are no peaks corresponding to glutamate or phospholipid functional groups. Moreover, in the case of G2 and G3 malignancy of adenocarcinoma lung cancer, the absence of an OH groups peak was noticed. The PCA-LDA analysis of differences in chemical compositions derived from selected FTIR spectral regions corresponding to protein and lipid vibrations. These IR ranges were used for all spectra obtained (control and cancers). The significantly distinct morphological areas were spectroscopically discriminated using unsupervised exploratory PCA. Therefore these areas can be analysed separately to determine the biochemical markers that differentiate control tissues, as well as cancerous lung tissues. Moreover, sensitivity and specificity were calculated not only for PCA-LDA results for healthy tissues and each type of cancer but also for every sample of each. These results produced information where, by using sensitivity and specificity, it is possible to distinguish not only between cancerous and non-cancerous tissues but also to identify different stages of the same cancerous tissues. Our results showed that the sensitivity of our model is between 78% and 99%, and the specificity between 65% and 99%. Summarizing, it seems that FTIR spectroscopy is a valuable tool to classify lung cancer and to determine the degree of its malignancy.

Spectroscopy Group at the University of the Basque Country

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The structural elucidation of molecular systems is a vastly explored aspect of science, as evidenced by the wide variety of techniques devoted to the task. In particular, high-resolution gas phase spectroscopy is able to unveil subtle structural and dynamical effects directly related to the chemical physical properties exhibited by a system, by isolating it from interactions with solvent or crystal packing. Moreover, by coupling these techniques with supersonic expansions, we can access the native conformational and aggregation preferences of molecules and intermolecular complexes.

The Spectroscopy Group at the University of the Basque Country (UPV/EHU) and the Biofisika Institute (CSIC-UPV/EHU) has built several microwave spectrometers. In our group, we have a chirped-pulsed FT-microwave spectrometer (CP-FTMW) equipped with a customized multi-valves system,[1] and a cavity based FT-MW spectrometer coupled with an UV ultrafast laser vaporization system.[2,3] Both set-ups are cutting-edge in the field of microwave spectroscopy. In addition, the Spectroscopy Group has strong collaborations with Prof. Corzana (Universidad de la Rioja), Dr. Çarçabal (Institut des Sciences Moléculaires d'Orsay) and Dr. Fernández (Universidad del País Vasco). These interdisciplinary collaborations allow us to investigate different biological and astrophysical topics since they grant us access to custom-made samples and various instrumentations and methodologies.

In order to illustrate our strategy, we present recent results focused on solving various structural problems of Chemistry at the molecular level. In particular, the conformational landscape of large clusters and biomolecules, including sugars, glycopeptides and drugs have been studied by our group recently.[3–6]



Figure. Microwave facilities available in Dr. Cocinero's Group at the University of the Basque Country (UPV/EHU).

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Spectroscopic characterization of the unsaturated Hydrocabons C_3H and C_5H using highly correlated ab initio methods

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Unsaturated carbon chains and hydrocarbons can play important roles in the chemical evolution of the interstellar sources. They can be considered as building blocks of large carbon species. Charged chains are reactive species that can participate in many chemical processes at low temperatures.

We present state-of-the-art ab initio calculations focused to the determination of equilibrium structures and spectroscopic parameters corresponding to various electronic states of the C_3H and C_5H chains containing an odd number of carbon atoms. Both species C_3H and C_5H present various isomers that can be linear or cyclic forms. All of them show non-zero dipole moments that can help their identification. Some of them are relatively stable structures.

Because, astronomers have dedicated special attention to the charged species during the last years, calculations of cations and anions are also provided. For all the cases, neutral, negative and positive charged species, excitations to the low electronic states are determined. We provide electron affinities and ionization potentials. Spin-orbit effects are predicted. The employed methodology was first used to describe other carbon chains containing even number of atoms [1–3]

P16.

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Broadening and shifting coefficients of rovibrational lines of HCl perturbed by He in the fundamental and the first overtone regions

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We present new data obtained using a modern high-resolution FTIR technique on He-broadening and shifting coefficients for the spectral lines for the fundamental and the first overtone vibration-rotation absorption bands of the HCl molecule. [1]

The both bands were recorded simultaneously by using a 20 cm stainless cell with sapphire windows and a Bruker IFS 125HR Fourier spectrometer with a resolution of 0.007 cm^{-1} . The pressure of He was kept in the range of 1–5 atm. Resulting 47 spectra allowed us to evaluate the line parameters in a large interval of J : $J_{\text{max}} = 15$ for the fundamental band and $J_{\text{max}} = 11$ for the overtone band. Most of the values, especially for the overtone transition, are novel.

All observed rovibrational lines have hypsochromic (blue) shift, which is a typical behavior upon collisions with helium. We did not register any statistically significant difference between the broadening and shift coefficients for H^{35}Cl and H^{37}Cl within our experimental uncertainty. The results are compared with existing literature values, the data for other hydrogen halides perturbed by helium [2] and HCl in mixture with other collision partners [3–6].

Acknowledgment. The study was supported by Russian Foundation for Basic Research [grant number 18-03-00520]. The spectra were recorded in the resource center 'Geomodel' of Saint Petersburg University. The PTB contribution was related to the EUMETRISPEC-initiative (EUMETRISPEC.org) funded under the European Metrology Research Programme.

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Predissociation of the B state of S₂: measurements and modeling

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Photoabsorption cross sections for the strong, predissociating vibrational bands, $v > 10$, in the S₂ B $^3\Sigma^-_u - X^3\Sigma^-_g(v,0)$ system were measured in a radio-frequency discharge through H₂S seeded in helium and in a two-temperature sulfur furnace, at temperatures of 370 K and 823 K, respectively. S₂ column densities were determined in each source by combining experimental line strengths in low- v non-predissociating B – X bands ($v < 7$) with calculated line f -values based on measured radiative lifetimes and calculated branching ratios. The broad-band capabilities of two vacuum-ultraviolet Fourier-transform spectrometers allowed for simultaneous recordings of both non-predissociating and predissociating bands, thus placing the predissociating-band cross sections on a common absolute scale. The bands studied ($11 \leq B(v) \leq 27$) exhibit varying degrees of diffuseness, with corresponding predissociation line widths ranging from 4 cm⁻¹ to 60 cm⁻¹. The experimental cross sections and measured line width patterns are used to inform a coupled-channel Schrödinger-equation model of predissociation in the B $^3\Sigma^-_u$ state of S₂. Just as in the analogous case of O₂, the B(v)-state predissociation in S₂ is caused principally by spin-orbit interactions with $^3\Pi_u$, $^1\Pi_u$, $^5\Pi_u$, and $^3\Sigma^+_u$ states. An inner limb crossing with B'' $^3\Pi_u$ is responsible for the predissociation of B($v = 11$) and provides a significant, slowly-varying contribution for B($v > 11$). Outer crossings with the $^1\Pi_u$, $^5\Pi_u$, and 2 $^3\Sigma^+_u$ states are responsible for oscillatory contributions to the predissociation widths, with first peaks at $v = 13, 20$, and 24, respectively, with the $^5\Pi_u$ contribution dominant.

Resonant two-photon ionization and mass-analyzed threshold ionization spectroscopy of 2,4-Difluoroanisole

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We report the vibronic and cation spectra of 2,4-difluoroanisole (24DFAN), recorded by using the resonant two-photon ionization and mass-analyzed threshold ionization spectroscopic techniques. The band origin of the $S_1 \leftarrow S_0$ electronic transition of 24DFAN appears at $35556 \pm 2 \text{ cm}^{-1}$; and the adiabatic ionization energy is determined to be $67568 \pm 5 \text{ cm}^{-1}$. The cation spectra were recorded by ionizing via the 0^0 , X^1 , τCH_3 , 15^1 , $9a^1$, and $6a^1$ levels in the electronically excited S_1 state. This allowed us to investigate the change in molecular geometry upon ionization and to detect more active vibrations of the cation.

The spectral assignment was made by comparing the present experimental data of 2,4-difluoroanisole with those of anisole, 2-fluoroanisole, and 4-fluoroanisole, 3,4-difluoroanisole, 2,4-difluorophenol and 2,4-difluoroaniline and the predicted values from the B3PW91/6-311++G(d,p) calculations. The observed active vibrations of 24DFAN in the S_1 and cationic ground D_0 states include methyl torsion, substituent-sensitive out-of-plane and in-plane ring bending and deformation modes. Comparison of the present data with those of fluorine substituted anisole, phenol, and aniline reveals the effect of fluorine substitution and additivity rule on electronic transition and molecular vibration. This enables us to have insights into ring-substituent and through-space substituent-substituent interactions.

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Keywords: 2,4-difluoroanisole, resonant multiphoton ionization, threshold ionization, cation spectra

High precision spectrum of the second overtone of $^{12}\text{C}^{16}\text{O}$

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CO is the second most abundant molecule in the universe. Precise spectrum of the carbon monoxide molecule is great importance in astrophysical observation and in the test of the quantum chemistry model. Thirty-nine ro-vibrational transitions of $^{12}\text{C}^{16}\text{O}$ in the second overtone band were measured by a comb-locked cavity ring-down spectrometer [1]. The line positions were determined with sub-kHz accuracy, or relatively 10^{-12} level. Improved molecular constants were obtained for the ground and second-overtone vibrational states. The calculated pure rotational line positions agree with the experimental values recorded by lamb-dip spectrometer within the experimental uncertainties. By comparing the calculated and experimental results, we present perspectives of the precision spectroscopy of the carbon monoxide molecule in the determination of the atom mass of ^{17}O by the Dunham-Watson model with first-order Born-Oppenheimer breakdown parameters.

CO₂-broadening and shift coefficients in the ν_3 and $\nu_2+(\nu_4+\nu_5)^0$ bands of acetylene

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The absorption spectra of the mixture of C₂H₂ and CO₂ at different partial pressures of both gases have been recorded at room temperature in the 3 μ m region using the Bruker IFS 125 HR FTIR spectrometer. The multispectrum fitting procedure has been applied to these spectra to recover the broadening and shift parameters of the acetylene spectral lines. The CO₂ broadening and pressure induced shift coefficients for 119 lines of the ν_3 and $\nu_2+(\nu_4+\nu_5)^0$ bands of acetylene have been derived. The rotational dependence of the values of these coefficients is discussed. The comparison of the obtained coefficients to those published by other authors for the ν_3 and $\nu_2+(\nu_4+\nu_5)^0$ bands is performed.

The *ab initio* line-shape calculations for purely rotational transitions in the CO–N₂ system

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Collisional line-shape effects play an important role in optical spectroscopy. Molecular collisions manifest as a perturbation of the optical line shapes. Proper treatment of these effects is important to reach high accuracy in spectroscopy-based optical metrology [1,2]. The CO–N₂ system is of particular importance for terrestrial atmospheric measurements. Here we report the first line-shape parameters for this system based on quantum scattering calculations performed on an accurate *ab initio* potential energy surface (PES) [3].

The four-dimensional PES [3], with the interatomic distances in N₂ and CO set to the experimental values (1.09768 and 1.128323 Å, respectively [4]) is used. The interaction energies are calculated with the coupled-cluster CCSD(T) method and Dunning's aug-cc-pVQZ basis set extended further with midbond functions for more than 10 100 *ab initio* points, corresponding to 12 values of θ_{N_2} , 13 values of θ_{CO} in a range of 0–180°, 5 values of ϕ in a range of 0–90° and 14 values of R in a range of 4–40 a₀. The calculated PES is expanded over bispherical harmonics [5] leading to 205 radial coupling terms. The close-coupling equations are solved for a wide range of kinetic energies using the MOLSCAT code [6]. The calculations of generalized spectroscopic cross sections are performed for several purely rotational lines from the R branch. Finally, the standard pressure broadening and shifting coefficients are obtained. The data provided through this investigation can be used for upgrading the HITRAN database [7] and the HITRAN Application Programming Interface (HAPI) [8].

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Spectroscopic study of the $7^1\Pi_u$ and $7^1\Sigma_u^+$ states of Rb_2 molecule

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Rubidium dimers are relatively easy to produce and observe experimentally but difficult for theoretical description, with a total of 74 electrons making in particular all-electron ab-initio treatment ineffective. Yet surprisingly, the theoretical knowledge of excited electronic states of this molecule is to date considerably larger than information provided by experiments [1]. To fill the gap between theory and experiment and to test the quality of theoretical description in the range of excitation energies close to the limits of calculations, we investigated two highly excited electronic states of Rb_2 , $7^1\Pi_u$ and $7^1\Sigma_u^+$.

Both states were observed in excitation spectra through transitions from the ground $X^1\Sigma_g^+$ state of rubidium dimer, using two-laser polarisation labelling spectroscopy technique [1]. Vapour containing Rb_2 molecules was produced by heating metallic rubidium (natural isotopic composition) to about 500 K in a heat-pipe oven in a presence of a few Torr of argon buffer gas. The spectra were recorded in the region 27000 – 29400 cm^{-1} with both resolution and accuracy slightly better than 0.1 cm^{-1} . In this region we identified more than 800 transitions to the $7^1\Pi_u$ state and 400 transitions to the $7^1\Sigma_u^+$ state, the frequencies of which were converted to energies of rovibrational levels in both states using the precisely known molecular constants of the ground state [2]. Observation cover the lowest 47 and 21 vibrational levels in the $7^1\Pi_u$ and $7^1\Sigma_u^+$ states, respectively. The spectroscopic parameters and potential energy curves for both states will be presented and compared with the state-of-the-art theoretical predictions.

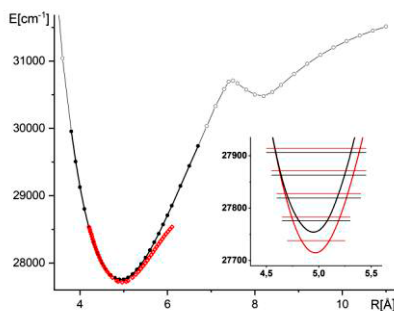


Figure caption: The experimental potential curves of the electronic states of Rb_2 investigated in this work: the RKR curve for the $7^1\Sigma_u^+$ state (red diamonds) and the pointwise IPA curve for the $7^1\Pi_u$ state (black circles connected with solid line). Open circles denote points of the potential virtually unaffected by the experimental data. The inset displays relative position of the lowest vibrational levels of both states (for $J=0$), illustrating why no strong interaction between both states have been observed despite the apparent similarity of their potential curves.

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The $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ absorption spectra at 296 K and 200 K in the range between 6600 and 12000 cm^{-1}

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The $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ absorption spectra in the range between 6600 and 12000 cm^{-1} have been recorded at 296 K and 200 K by the Fourier spectrometer IFS – 125M at pressures from 11 to 300 mbar, and spectral resolution 0.03 cm^{-1} . Multi-pass cell with a length of 60 cm and 44 passes was used, which provided the pathlength of 2640 cm and threshold sensitivity to absorption of the order of 10^{-8} cm^{-1} . Empirical values of the lower state energy level were derived from the intensity ratios of the lines measured at 200 K and 296 K. Line assignment of the $\nu_2 + 2\nu_3$ band of the $^{13}\text{CH}_4$ molecule and the $3\nu_3$ band of the $^{12}\text{CH}_4$ molecule was performed. The parameters of Voigt contour (the line center, intensity, self-broadening coefficient and self-shift coefficient) were determined using multi-fitting procedure at 296K.

The work partly was supported by the Russian Scientific Foundation (Grants № 17–17–01170).

Study of hydrates of verbenone by microwave Fourier transform spectroscopy and computational chemistry

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The first studies of hydrates of aldehydes and ketones were performed by Lovas and Lugez on the formaldehyde – water system in 1996 [1] and by Melandri et al. in the cyclobutanone – water system in 2005 [2]. More recently, Pérez et al. investigated the interaction of water with camphor [3]. They were able to characterize a trihydrate constituted by a chain of three water molecules around the camphor molecule. We present here our results on the verbenone – water system. Verbenone is a bicyclic ketone, with an intracyclic carbon – carbon double bond conjugated with the carbonyl moiety. It could be interesting to investigate if the delocalization of p -electrons within verbenone influences or not the formation of hydrates.

The rotational spectrum of verbenone being already known [4], we started with the study of the hydrates. The structures of two monohydrates, two dihydrates and four trihydrates of verbenone were optimized at the DFT B3LYP–D3BJ / def2–TZVP and *ab initio* MP2 / 6–311++G(d,p) levels. Experimentally, a gas mixture of verbenone – water – neon was expanded into the cavity of a Balle–Flygare type Fourier transform microwave spectrometer operating in the 2 – 20 GHz frequency range. Scanning around the predicted frequencies of each hydrate, we were able to find the spectral signatures of the two mono- and two dihydrates, and of the lowest energy conformer of the trihydrate. A similar study replacing normal water by ^{18}O labeled water allowed the identification of the spectra of all possible isotopomers, leading to the calculation of the substitution coordinates of water oxygen atoms, and of the effective structure of the water molecules arrangements around verbenone. A comparison of our results with those obtained by Pérez et al. on camphor is presented.

The present work was funded by the French ANR Labex CaPPA through the PIA under contract ANR-11-LABX-0005-01, by the Regional Council Hauts de France, by the European Funds for Regional Economic Development (FEDER), and by the French Ministry of Higher Education and Research. It is a contribution to the CPER research Project CLIMIBIO.

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Study of the H₂O–N₂ line broadening and shifting in the region of 16500–17000 cm⁻¹

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The broadening of the spectral lines of water vapor by air and nitrogen pressure is of great interest for various atmospheric problems. The spectra have been recorded with a spectral resolution of 0.05 cm⁻¹ by a Fourier transform spectrometer using high luminance LED light source. A high signal-to-noise ratio ($S/N \approx 10\,000$) permitted to analyze the lines with intensities of 1.54×10^{-23} to 2.0×10^{-26} cm/molecule. The N₂-broadening and shifting coefficients of the water vapor lines in the region of 16600–17000 cm⁻¹ were obtained using multi-spectrum fitting. The results of the measurements are compared with calculations using the semi-empiric method, which is based on the impact theory of broadening, and includes the correction factors whose parameters are determined by fitting the broadening coefficients to the experimental data. The method is further developed by using anharmonic wavefunctions in the estimates of line profiles. This approach explicitly takes into account all scattering channels induced by collisions. In principle, the use of the accurate wave functions, obtained from global variational calculations, extends the applicability of the method up to dissociation energy of molecule.

The work was supported by the Russian Foundation for Basic Research (Grants No. 16–43–700492, 17–52–16022_a).

Rotational-predissociation double resonance spectroscopy of the He-HCO⁺ complex

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Cation-Helium complexes are interesting spectroscopic systems due to the floppy bond of the helium atom. He-HCO⁺ is a particularly prominent test system, as it is linear and has a ¹Σ ground state.

So far experimental data have been limited to infrared studies on the ν₁ C-H stretching mode of He-HCO⁺ [1].

In this work, we present for the first time high-resolution rotational data for this complex, applying a novel rotational-predissociation double resonance method.

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Combined PGOPHER analysis of bands in the 1st positive system of N₂, 4500 – 15500 cm⁻¹

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Dennis Tokaryk³

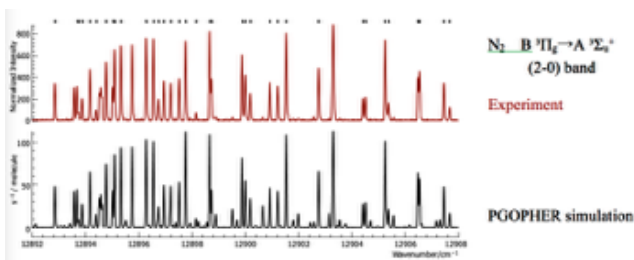
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Boesch and Reiners recently pointed out [1] that spectral line lists for nitrogen gas could provide useful wavelength calibration for high-resolution astrophysical spectrographs. Boesch and Reiners recently pointed out [1] that spectral line lists for nitrogen gas could provide useful wavelength calibration for high-resolution astrophysical spectrographs. They recorded and reported extensive spectra in the infrared 4500–11000 cm⁻¹, revisiting notably the first positive system of N₂ (A³Σ_u⁺ – B³Π_g, B¹Σ_u⁺ – B³Π_g and W³Δ_u – B³Π_g), and the Meinel bands of N₂⁺, since there is no electronic record of spectra recorded in the late 1970's [2,3]. Working at slightly shorter wavelengths with an intracavity experiment designed to study discharge-formed species, we saw lines of the first positive bands of N₂ in absorption as impurity contributions, and realized that N₂ can provide spectral calibration for the Ti:sapphire based Vernier frequency-comb spectrometer [4]. We therefore recorded a new FT 'reference' N₂ emission spectrum. This spectrum (nominal resolution 0.023 cm⁻¹) was corrected for instrumental intensity response, and is available in ascii format.

The N₂ bands recorded in [1] have been analysed together with this spectrum using the PGOPHER program [5], providing constants for the A³Σ_u⁺, B³Π_g, B¹Σ_u⁺ and W³Δ_u states, automatically rejecting blends to optimize parameter reliability. Final parameters are consistent with those reported in refs [2,3], but better defined, and from a more standard Hamiltonian. They allow a reference spectrum to be constructed for different conditions (temperature, lineshape, resolution), if the raw, Doppler-limited measurements are unsuitable for comparison. The figure below shows part of the N₂ emission spectrum, compared with PGOPHER simulation. The tick marks at the top of the plot indicate transitions retained (by automatic selection) in the fit. Note that the excluded transitions – including some strong features – are also well modeled.



Keywords: Astrophysics/Atmospheric VIS/UV Gas Phase/jets Small molecules

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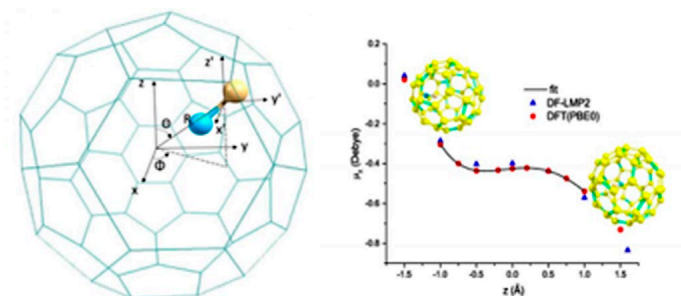
Properties of HF@C₆₀ endofullerene from first principles

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Endofullerenes, fullerenes with an atom or molecule inside, have attracted significant attention during the past decade [1, 2]. Of particular interest is small dipolar molecules inside the buckyballs. The materials composed of such systems could have ferroelectric properties. We have chosen to study HF@C₆₀ system (Fig. 1), first synthesized in 2016 using “molecular surgery” [3] technique. The potential energy (PES) and dipole moment (DMS) surfaces for the case of *I*_h symmetry of C₆₀ (rigid cage) were obtained based on *ab initio* and DFT computed data (see Fig. 2 for example computation of dipole moment). The cc-pVTZ basis set was employed throughout the work. Using these PES and DMS of HF@C₆₀ we were able to compute translation–rotation energy levels and molecular polarizability (temperature-dependent). Also, a model potential was suggested that takes into account the splitting of *j*=1 rotational level of HF. This splitting was observed in experiment [3].



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High sensitivity Cavity Ring Down Spectroscopy of the $\nu_1+4\nu_3$ band of NO_2 near $1.34\ \mu\text{m}$

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The very weak $\nu_1+4\nu_3$ *B*-type absorption band of nitrogen dioxide ($^{14}\text{N}^{16}\text{O}_2$) is newly detected by high sensitivity continuous wave-cavity ring down spectroscopy between 7376 and $7550\ \text{cm}^{-1}$. The noise equivalent absorption of the recordings is $\alpha_{\text{min}} \gg 1 \times 10^{-10}\ \text{cm}^{-1}$. The $\nu_1+4\nu_3$ band is the highest energy *B*-type absorption band of NO_2 detected so far by absorption within the ground electronic state. More than 500 lines are assigned with rotational quantum numbers N and K_a up to 50 and 7, respectively, what corresponds to 1117 spin-rotation-vibration transitions. No resonance perturbation of the spectrum was evidenced. The fitted set of the effective Hamiltonian parameters reproduces the observed line positions with an *rms* of $3.7 \times 10^{-3}\ \text{cm}^{-1}$. A selected set of the measured line intensities are used to determine the effective dipole moment parameters including the Herman-Wallis type parameters describing the line intensities of this band. The *rms* deviation of the fit is 15.24%.

Laser absorption spectroscopy of methane at 1000 K between 1.75 and 1.3 μm

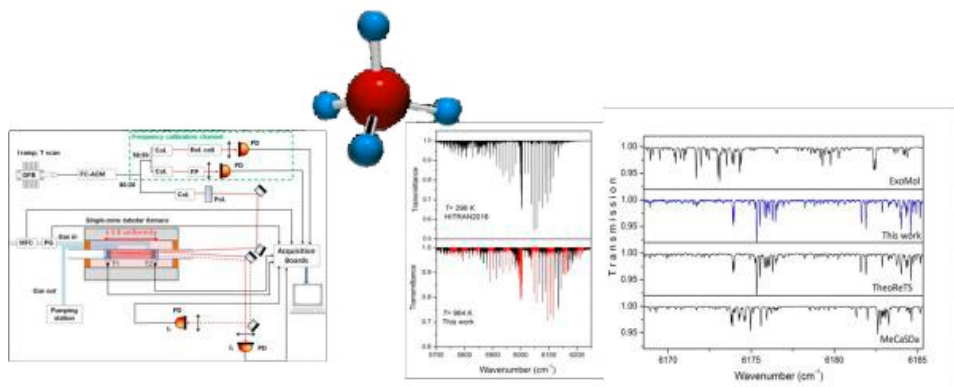
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A tubular furnace is combined with a diode laser spectrometer to record the high temperature near infrared absorption spectrum of methane at a pressure of 80 Torr. The investigated spectral range covers the 5693–6257 cm^{-1} range of the tetradecad dominated by the $2\nu_3$ band near 6000 cm^{-1} [1] and the icosad between 6800 and 7700 cm^{-1} . The spectra were recorded at 523 K and 773 K in both regions and additionally at 964 K in the tetradecad region. At 964 K, lines with intensity larger than 5×10^{-24} $\text{cm}^2/\text{molecule}$ were measured.

As a result of the high temperature, high- J rovibrational transitions up to $J \approx 20$ and hot bands are identified in the spectrum. The recorded spectra provide tests of various methane line lists recently released in the literature: HITRAN2016, experimental list derived from emission spectra, the MeCaSDa empirical line list and the TheoReTs and ExoMol theoretical line lists. Overall, the agreement with the TheoReTs line list is found to be very good, in particular in the tetradecad region.



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Double resonance rotational spectroscopy of $\text{CH}_3^+ - \text{He}$

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A new double resonance method combined with cryogenic trapping is applied to the $\text{CH}_3^+ - \text{He}$ system. For this purpose, the ions are trapped in a 22-pole ion trap, cooled down to 4 K and are exposed to two radiation sources. On double resonance, a mm-wave leads to excitation into a rotationally excited state followed by IR vibrational excitation into a dissociative state. The vibrational spectra of the C–H stretching motions ν_1 and ν_3 have been recorded and used for predissociation. In total, 24 *P* and *R* branch transitions are resolved for the antisymmetric band (ν_3) and ten partly resolved features are measured for the symmetric band (ν_1). Both spectra show perturbations which seem to be characteristic for these complexes. The pure rotational ground state transitions are highly resolved ($\sigma \sim 3$ kHz), revealing unexpected splittings for the $K = 1$ transitions. This splitting is most probably given by the large amplitude motion of the Helium atom.

The absorption band of nitrogen dioxide ($^{14}\text{N}^{16}\text{O}_2$) by CRDS near 6000 cm^{-1}

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The high resolution absorption spectrum of the NO_2 molecule is recorded between 5800 and 6000 cm^{-1} by high sensitivity cavity ring down spectroscopy (CRDS). Positions and intensities in the range from 2×10^{-28} to $4 \times 10^{-23}\text{ cm}^2/\text{molecule}$ are derived from the line profile fitting for more than 7500 lines. The spectrum is dominated by the transitions of the $103-000$ vibrational band centered at 5984.704 cm^{-1} . The spectrum is assigned and modeled using an effective Hamiltonian which explicitly takes into account a spin-rotational interaction and interaction of the (103) bright state with three “dark” states: (122) , (080) and (410) . The n_1+3n_3 band was already analyzed by Fourier transform spectroscopy in Ref. [1], where resonance interactions between the (103) state and the (122) , and (080) “dark” states at 5898.940 and 5965.610 cm^{-1} , respectively – were taken into account. More than 3000 lines are presently assigned with rotational quantum numbers N and K_a up to 57 and 13, respectively (In Ref. [1], 1147 transitions were identified with maximum N and K_a values of 47 and 8, respectively). The measured line positions are reproduced with an *rms* of 0.0024 cm^{-1} by variation of 39 parameters of the effective Hamiltonian. About 80 transitions reaching the highly excited (080) bending upper state and borrowing their intensity from the resonance coupling with the $103-000$ band were assigned for the first time. The main parameters in the transition moment series are determined for the (103) vibrational state from the fitting of the measured intensities and the detailed synthetic spectrum is generated.

P1.23.

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Isolated small-amplitude fundamental embedded in a pure torsional bath: assignment and fit of the FIR and microwave spectra of the ν_{10} vibrational state of acetaldehyde.

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We present results of our analysis of the FIR spectrum of the ν_{10} vibrational state of acetaldehyde near 509 cm^{-1} . The analysis of the 509 cm^{-1} band involves energy levels that belong to the $\nu_t = 0, 1$ torsional states of the ν_{10} vibrational state and is accompanied by the assignment of microwave spectra of the $(\nu_{10}, \nu_{15}) = (1, 0), (1, 1), (0, 3), (0, 4)$ states of acetaldehyde, where the ν_{15} state corresponds to large amplitude torsional vibration in the molecule. The analysis employs a new program which was recently developed for fitting several isolated small-amplitude fundamentals embedded in a pure torsional bath in molecules like acetaldehyde, in which the frame has C_s symmetry and the methyl top has C_{3v} symmetry. In the fit the new assignments of the transitions with J up to 50 are combined with data available in the literature for the $\nu_t = 0, 1, 2, 3, 4$ torsional states of the molecule [1,2]. Our results provide significant progress in comparison with previous fitting attempts [1] for the ν_{10} band of acetaldehyde near 509 cm^{-1} .

Acknowledgements: This work was done under support of the Volkswagen foundation. The assistance of Science and Technology Center in Ukraine is acknowledged (STCU partner project #P686).

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The high resolution spectrum of $^{14}\text{ND}_3$ in the far-infrared

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Triply deuterated ammonia is the prototype molecule of the multiply deuterated species containing nitrogen. Due to its astrophysical role, the spectroscopic characterization of its ground state (GS) and of the vibration energy patterns should be extended. The analysis of the vibration-rotation-inversion transitions from high resolution IR spectra of the $\nu_2/\nu_4/2\nu_2$ and $\nu_1/\nu_3/2\nu_4$ band systems has been reported in [1]. Recently, the pure inversion and rotation-inversion transitions in the GS [2] have been re-analyzed together with ground state combination differences from allowed and perturbation allowed ro-vibration transitions [3]. Accurate values of C , D_K and H_K constants in the s and a GS levels could be derived from the first time.

New spectra of the $^{14}\text{ND}_3$ have been recorded in the 65–1200 cm^{-1} range at an unapodized resolution of 0.00096 cm^{-1} , using the Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beam line, Canadian Light Source, Saskatoon, Canada. All the spectra were recorded at 298 K using a 2 m base multi pass absorption cell, set for 8 m, with 7 Pa of sample pressure, and 72 m, with 1.3, 13 and 133 Pa of sample pressures. The high sensitivity, resolution and enhanced signal to noise ratio of the new spectra will allow the detection of weak rotation-inversion transitions of $^{14}\text{ND}_3$ in the GS and in the low lying bending excited states, $\nu_2 = 1, 2$ and $\nu_4 = 1$. Eventually, the identification of very weak $\Delta J = 1$, $\Delta K = \pm 3$ $s \leftarrow s$ and $a \leftarrow a$ forbidden transitions will improve the accuracy of the K -dependent parameters. The preliminary results of this analysis will be presented.

P1.25.

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Line positions and intensities for the ν_3 band of 5 isotopologues of germane for planetary applications

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- 4) *Service de Chimie Quantique et Photophysique, C. P. 160/09, Université Libre de Bruxelles, 50 avenue F. D. Roosevelt, B-1050 Brussels, Belgium*
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Germane (GeH_4) is present in the atmospheres of the giant planets Jupiter and Saturn. The ongoing NASA mission Juno has renewed interest in its spectroscopy. The accurate modeling of which is essential for the retrieval of other tropospheric species. We present here the first complete analysis and modeling of line positions and intensities in the strongly absorbing ν_1/ν_3 stretching dyad region near 2100 cm^{-1} , for all five germane isotopologues in natural abundance. New infrared spectra were recorded, absolute intensities were extracted through a careful procedure and modeled thanks to the formalism and programs developed in Dijon. A database of calculated germane lines, GeCaSDa, is available online through the Virtual Atomic and Molecular Data Centre (VAMDC) portal (<http://portal.vamdc.org>) and at <http://vamdc.icb.cnrs.fr/PHP/gecasda.php>. GeH_4 will integrate the HITRAN database as molecule number 52.

The third and fourth torsional states of acetic acid

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Acetic acid is of intrinsic spectroscopic interest since several of its hindered internal rotation characteristics make it a well-suited molecule to test the performances of the methods applied to the analysis of internal rotation phenomena. Previous experimental investigations resulted in a thorough analysis of the $v_t = 0, 1, 2$ torsion–rotation transitions with J up to 79 and K_a up to 44[1]. In this study we present the results of investigation of the millimeter wave spectrum of the $v_t = 3$ and 4 excited torsional states of acetic acid. The data set found in the literature has been augmented by about 1900 new $v_t = 3$ and 4 transition frequencies in the 49 – 149 GHz range obtained in Kharkiv. The new measurements as well as the previous ones published earlier[1] were included in a global fit involving $v_t = 0, 1, 2, 3$, and 4 states of acetic acid. The RAM approach, successfully used in the past for this molecule, provided a weighted standard deviation of 1.2 for 17241 line frequencies using 107 parameters. In the presentation the details of this new study will be discussed.

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First detection of H_2^{36}S in the infrared region

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High-Resolution spectra of hydrogen sulfide have been measured with the Bruker IFS125HR Fourier transform Zürich prototype infrared spectrometer ZP2001, [1] which was modified to increase the optical resolution up to 0.00096 cm^{-1} . The recorded spectral region $600\text{--}5000\text{ cm}^{-1}$ have been analyzed with the GSCD method. For this purpose, rotational energy levels were obtained on the basis of microwave transitions from [2–3].

Parameters of the effective operators of the ground vibrational state were determined from the inverse problem solution.

Sample of hydrogen sulfide of 99.5% stated purity (Merck/Sigma-Aldrich AG) was taken in natural composition. For the spectra analysis of the least abundant, H_2^{36}S , isotopologue parameters of the effective Hamiltonian of ro-vibrational states, as well as, effective dipole moment parameters for corresponding bands, were predicted on the basis of isotopic substitution theory [4] and approved by extrapolation from H_2^{32}S , H_2^{33}S , H_2^{34}S isotopologues. As a result, 3 ro-vibrational bands of H_2^{36}S were analyzed for the first time.

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New electronic states in the spectra of TaH and TaD

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We have recorded electronic spectra of tantalum hydride (TaH) and deuteride (TaD) over the region 605–665 nm. The molecules were produced by sputtering tantalum in a hollow cathode source with a dilute mixture of hydrogen or deuterium in argon. The spectra were recorded by laser excitation spectroscopy at Doppler-limited resolution using a continuous-wave ring dye laser. We have identified a total of 10 different bands in TaH and 4 in TaD, all of which involve distinct excited electronic states. The various transitions originate from one of two low-lying electronic states, with $\Omega = 2$ or 0^+ .

Calculations by the Gordon group [1] and previous experimental work on the molecule in our group [2] agree that the $\Omega = 2$ state is largely derived from a $\delta^1\pi^1$, $^3\Phi_2$ state. The $\Omega = 0^+$ state, which is largely a mixture of $^3\Sigma^-$ and $^3\Pi$, is calculated to lie within 600 cm^{-1} of the $\Omega = 2$ state [1]. We are conducting dispersed fluorescence experiments with the aim of determining which of these two low-lying states is the true ground state. Preliminary results indicate the presence of a third state about 1400 cm^{-1} above the $\Omega = 2$ state, which may be the $\Omega = 1$ component of the mixed $^3\Sigma^- / ^3\Pi$ state. The various electronic states have been fitted by least-squares using a Hund's case (c) Hamiltonian. We will report term energies, rotational and centrifugal distortion constants, bond lengths and vibrational intervals for all of these states.

P1.29.

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Accurate first principles global calculations and isotopic effects on infrared spectra for phosphine PH₃ and hydrocarbons (CH₄, C₂H₄)

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Isotopic substitutions as H → D or even ¹²C → ¹³C have substantial consequences on molecular spectra. To interpret correctly the experimentally observed spectra of molecules in their natural abundances, it is essential to have realistic and reliable theoretical models.

There is much less information on assigned experimental spectra of rare isotopologues, particularly for the intensities. The corresponding line lists at medium spectral resolution could be provided by the *ab initio* theory and global nuclear motion variational calculations.

The aim of this work will be to study the effects of isotopic substitutions in PH₃, CH₄, and C₂H₄, on both line positions and line intensities, from nonlinear transformations and symmetry considerations. In case of phosphine we consider PH₂D, PHD₂ isotopologues [5], and ¹²C → ¹³C substituted species for the methane and the ethylene. All calculations are based on our recent *ab initio* potential and dipole moment surfaces [1, 2, 3] using variational normal mode calculations [4]. The corresponding line lists will be made available via the TheoReTS information system [6] (<http://theorets.univ-reims.fr>, <http://theorets.tsu.ru>).

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Vibrational dependence and prediction of line shape parameters for the H₂O–H₂ collisional system

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The Modified Complex Robert–Bonamy (MCRB) formalism was used to calculate the half-width, γ , and line shift, δ , for the H₂O–H₂ collision system at 14 temperatures between 200 and 3000 K for over 7 thousand rotational transitions for the rotation band, the (301)–(000) band and bands for ν_1 , ν_2 , and ν_3 with 1–4 vibrational quanta exchanged. The calculations include all complex terms, explicit velocity integration, and a potential composed of electrostatic, induction, London dispersion, and atom–atom (expanded to 20th order and rank 4) terms using the parameters of Renaud *et al.* [1], and ground state reduced matrix elements. These data were used to study the vibrational dependence of the half-width and line shift. It is shown that the H₂O–H₂ collision system is strongly off-resonance. The results demonstrate strong and unusual vibrational dependence.

The half-width and line shift data for different vibrational bands were used to develop a prediction routine for γ and δ . Following the work of Jacquemart *et al.* [2] and Gamache and Lamouroux [3], the expressions

$$\gamma[(\nu_1', \nu_2', \nu_3') \leftarrow (\nu_1'', \nu_2'', \nu_3'')] = I_{f \leftarrow i}^{\gamma} + A_{f \leftarrow i} (C_1 |\Delta \nu_1| + C_2 |\Delta \nu_2| + C_3 |\Delta \nu_3|)^{p_{\gamma}}$$

and

$$\delta[(\nu_1', \nu_2', \nu_3') \leftarrow (\nu_1'', \nu_2'', \nu_3'')] = I_{f \leftarrow i}^{\delta} + B_{f \leftarrow i} (C_1 |\Delta \nu_1| + C_2 |\Delta \nu_2| + C_3 |\Delta \nu_3|)^{p_{\delta}}$$

were used to predict the half-width and line shift where the powers p_{γ} , p_{δ} , and coefficients $I_{f \leftarrow i}^{\gamma}$, $A_{f \leftarrow i}$, $I_{f \leftarrow i}^{\delta}$, and $B_{f \leftarrow i}$ were determined by non-linear least-squares techniques. It is shown that the fits need to be made separately for bands with stretch–quanta exchanges and bend–quanta exchanges. From these fits, a prediction routine was developed that gives very reasonable results.

P1.31.

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Ab initio reduced matrix elements for H_2^{16}O : application to $\text{H}_2\text{O}-\text{H}_2$ line shape calculations via the modified complex Robert–Bonamy method

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The determination of the reduced matrix elements (RMEs) is an important part of the Modified Complex Robert–Bonamy (MCRB) calculations. Lamouroux *et al.* [1] used the *ab initio* wavefunction of Partridge and Schwenke [2] to determine these RMEs. In the same work, they also derived sums rules, which allow one to check the calculated RMEs. They show that for a state i , the sum of the square of the RME over all collisionally connected states equals one.

In this work, the sums rules have been applied to rotational states of a number of vibrational states. For a number rotational states the sum rules are obeyed, however for many others they do not give the correct sum. It is shown that the use of incorrect RMEs is a source of inaccuracy in the MCRB calculations, which significantly affects the determination the collisional half-width and the line-shift. Calculations, using the ground state and the vibrational dependent RMEs, were performed to show the influence of this spectroscopic effect.

It is shown that the best calculations of the line shape parameters are those using RMEs that obey the sum rules.

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Classical trajectory simulation of collision-induced absorption spectra

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Various theoretical approaches (see e.g. [1–4]) are used in order to simulate collision-induced absorption (CIA) spectra, reliable knowledge of which is required nowadays for planetary climate modeling. Among these approaches the use of classical trajectory simulation is particularly promising since it makes possible relatively cheap evaluation of the spectral profiles using presently available ab initio calculated potential energy (PES) and induced dipole (IDS) surfaces.

The goal of the current paper consists of development and numerical realization of the procedure that enables simulation of the rototranslational CIA band profile for interacting monomers of arbitrary symmetry. We start by constructing a classical intermolecular Hamiltonian in a chosen body-fixed frame. Then the equations of motion are derived along with the trajectory density function. Methods of computer algebra are used to ensure correct results. Finally extensive classical trajectory calculations are carried out to compute the resulting CIA spectrum. Markov chain technique is applied to generate a set of initial points properly distributed in the phase space.

Simple anisotropic CO₂–Ar prototype system was first taken as an example. The spectra for this system were considered recently in Ref. [4] using classical trajectory analysis, though the formalism in Ref. [4] is significantly at variance from our approach.

Our trajectory simulation for concrete molecular pairs is supported by extensive ab initio PES and IDS calculations on a grid of angles and intermolecular separations followed by their analytical fit.

P1.33.

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Atlas of experimental and theoretical high-temperature methane cross-sections from T=296 K to 1000 K in the mid-infrared range

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Spectra of hot methane were recorded at Old Dominion Norfolk University using a tube furnace, a quartz cell (optical path length of 50 cm) and a Bruker 120/125HR spectrometer. For each temperature, a total of 600 interferograms were recorded for both the sample and corresponding background at a resolution of 0.02 cm⁻¹. The experimental setup is similar to that of ref [1]. In this work, we obtained experimental absorption spectra at eight temperatures T= 296 K, 400 K, 500 K, 600 K, 700 K, 800 K, 900 K and 1000 K. These experimental records cover the mid infrared range from 5400 to 9000 cm⁻¹. We have converted this to the atlas of T-by-T absorption cross-sections for the methane polyad corresponding to the Tetradecad, Icosad and Triacotad excluding some particular intervals strongly contaminated by water. On the theoretical side the spectra were simulated from ab initio based Reims-Tomsk line list for the same experimental conditions. It has been constructed by global variational calculations from potential energy and dipole moment surfaces followed by empirical line position corrections deduced from previously published cold T analyses as described in [2–4] (and references therein). The comparisons showed very good overall agreement between observations and the theory at least at the medium spectral resolution. Preliminary assignments resulted to identifications of more than 10000 lines in each T spectrum. A full set of the theoretical absorption cross-sections is also included in the Atlas. The data could be of major interest for interpretation of current and future astronomical observations [5].

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High-resolution laser spectroscopy of nitrogen dioxide in the region of 14500–16800 cm⁻¹

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The nitrogen dioxide (NO₂) is one of the important stable free radicals to investigate the intra-molecular interactions of polyatomic molecules. The visible absorption spectrum shows complexity which comes from the fine structure due to the spin $S=1/2$ of the unpaired electron and the hyperfine structure due to the nuclear spin $I=1$ of the ¹⁴N atom. Several previous studies examined the hyperfine structures of $N=1$ levels of the excited electronic states, and reported that the hyperfine interaction constants correlated with the state mixing of the X and A states. In this study, we observed hyperfine-resolved high-resolution fluorescence excitation spectra of the $A\ ^2B_2 \leftarrow X\ ^2A_1$ electronic transition of ¹⁴NO₂ radical in 14500–16800 cm⁻¹ energy region by crossing a single-mode laser beam perpendicular to a collimated molecular beam [1]. In the observed region, the $^oR_0(0)$ lines ($k = 0$, $N = 1 \leftarrow 0$ transition) were observed for more than 80 vibronic bands, and their hyperfine interaction constants; the Fermi contact interaction constants and the dipole-dipole interaction constants were determined. The determined Fermi contact interaction constants in the 14500–16100 cm⁻¹ region were found to be intermediate in magnitude between those in lower and higher energy region reported by other groups. On the other hand, a sharp decreasing of the Fermi contact interaction constant was found in 16 200 – 16 600 cm⁻¹ region, and it may be caused by the interaction with the dark $C\ ^2A_2$ state.

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Modified complex Robert–Bonamy calculations including line coupling on the H₂O–N₂ and CO₂–N₂ molecular systems

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The Modified Complex Robert–Bonamy formalism [1,2] has been recently refined by Ma *et al.* [3] to go beyond the isolated line approximation by introducing the effect of the line coupling. The modification leads to off-diagonal terms in the $S_{2,\text{middle}}$ operator. This coupling effect has been successfully implemented in our line shape code and applied to the H₂O–N₂ and CO₂–N₂ collisional systems. The half widths and the line shifts calculations, considering the coupling effect, include all complex terms, explicit velocity integration and an extract trajectory model. The intermolecular potential is comprised of electrostatic, atom–atom (expanded to 20th order and 4th rank), induction and London dispersion terms.

Depending on the transition and collisional system, the effects of line coupling effect go from being negligible to large. The addition of line coupling to the calculation reduced the value of the half-width, sometimes substantially. More importantly, the reduction is in the direction of the measured values. For example, in early MCRB calculation, Gamache *et al.* [4] had to set the CO₂ quadrupole moment “at the lower error estimate” in order to reproduce measurements. This reduction is no longer needed when line coupling is included. The CO₂–X intermolecular potential adjustments (X = N₂, O₂, air, CO₂) will be reinvestigated with calculations employing line coupling.

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Temperature dependence of line broadening coefficient of chloromethane diluted in carbon dioxide

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The chloromethane is one of the primary chlorine ion source in the upper atmosphere, and is on the watch list of the World Meteorological Organization regarding climate change monitoring [1]. It originates both from natural sources, such as biomass burnings or tropical forests, and from human industrialization [2,3].

In this work, we studied line broadenings of chloromethane diluted in carbon dioxide in the $^{\circ}\text{P}$ branch of the ν_1 band at low temperature (200K to room temperature). The spectra were recorded with a high resolution diode laser spectrometer.

To retrieve the broadening coefficients, we fitted theoretical line shape models on the experimental profiles. We used the common Voigt profile, as well as the Rautian and Sobel'man and the Galatry profiles. We then computed the temperature dependence coefficients.

P1.37.

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A room-temperature HCN line list with a new dipole moment surface

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A new *ab initio* high accuracy dipole moment surface is constructed for the HCN system. The IC-MRCI all-electrons method was used to compute dipole moments. 902 dipole points were computed using external field method and fitted using a polynomial functional form with a standard deviation less than 10^{-5} Debye. The refined potential energy surface (PES) from our previous study [1] was also improved and giving energy levels accurate to better than about 0.03 cm^{-1} .

We report improved calculated intensities for all the fundamental bands of HCN. The standard deviation of calculated intensities for transitions within the ν_1 and ν_2^0 bands from the experimental values is reduced to about 1%. Our key improvement is for ν_3 stretching transitions. The P-branch intensities in our last calculated line-list [2] differed from the experimental ones by 36%; our new calculations have a corresponding difference of about 21%. The location of the second R-branch intensity minimum is also improved.

Our ultimate goal is to calculate a high-level global high-temperature line-list for HCN/HNC system. Our new DMS and the previously reported PES [1,3] represent an important step on towards this goal. Our room-temperature HCN line list will both improve the accuracy with which transition intensities are predicted and cover a wider wavenumber range than the previous line list [2], which was based on combination of experimental and recent *ab initio* calculated data [4].

The reported study was funded by RFBR according to the research project № 18-32-00698.

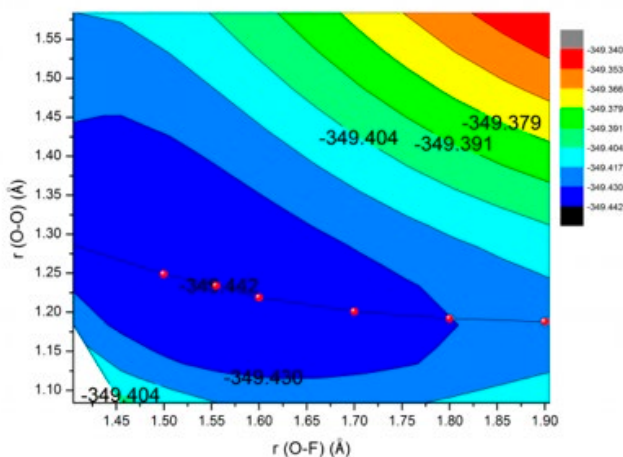
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Quantum chemical characterisation of difluorine peroxide FOOF

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Dioxygen difluoride has been known for a long time to possess very unusual equilibrium geometry, whose theoretical characterization was considered a "nightmare for theoreticians". In the present work we have identified the reason for this resistance: the flatness of the OO, and more important OF, stretching potential energy curves, which make it difficult to localise the global minimum. It is not related to the weak multi-reference character. Using high-level CCSD(T)-F12/VTZ-F12 ab initio theory, the global minimum has been properly located and vibrationally averaged bond lengths obtained. These vibrationally averaged parameters agree with experimental data to within 0.01 Å. We have then simulated the IR and UV spectra, which compare well with experimental data and permit identification of the observed transitions. The problem that has persisted for more than forty years, highlighted in a recent review article by Oberhammer titled "Gas phase structures of peroxides: experiments and computational problems", has been resolved.



P1.39.

On the consistency of absolute ozone intensities in MW, 10 and 5 micron ranges from *ab initio* predictions and laboratory observations

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The problems of the consistency of the ozone intensity data of the ozone molecule in various spectral infrared regions including 10 μm , 5 μm and the UV cross-sections has been subject of many discussion in the past decades but is not yet completely solved [1–6]. We present *ab initio* calculations for absolute line intensities in the most important absorption regions: in the microwave (rotational transitions), in the 10 micron range (stretching fundamentals) and in the 5 micron range (first triad of stretching overtone and combination bands) using our potential energy [6] and dipole moment [7] surfaces. The estimated intensity accuracy of our theoretical list is expected to be about 1% or even better. Our *ab initio* predictions will be compared to the recent yet unpublished FTS measurements of GSMA Reims group covering the ranges 800 – 2300 cm^{-1} as well as to existing databases (S&MPO [8], HITRAN [9], GEISA [10], JPL [11]). Origins of various error sources and data inconsistencies will be discussed. We acknowledge the support from LEFE CHAT CNRS French program and from Mendelevy funding TSU grant.

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Rotational and vibrational dependences of line half-widths for CO confined in silica aerogel

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Molecules in nanopores are detected both in gas phase and adsorbed on the inner surface [1]. Contrary to adsorbed molecules, gas-phase ones freely move inside nanopores and collide with their walls, and the absorption spectra of these molecules have a fine rotational structure. Inside nanopores, spectral line parameters of molecules are induced predominantly by collisions with their walls. In papers [2, 3] different rotational dependences for CO confined in nanoporous materials with different structures were obtained.

In this report we present study of absorption spectra of carbon monoxide confined in silica aerogel with the density of 0.058 g/cm^3 . The measurements were performed within 2000 – 2300 and 4100 – 4400 cm^{-1} spectral regions at room temperature using Bruker IFS 125HR Fourier spectrometer. Dependences of the HWHM values on rotational and vibrational quantum numbers were studied and compared with data available in literature [2–4].

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Measurements and calculations of H₂- broadening and shift parameters of water vapor transitions in 6700–9000 cm⁻¹ spectral region

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Hydrogen pressure induced broadening and shift coefficients for water vapor absorption lines in the 6700–9000 cm⁻¹ region have been measured and calculated. The spectra were recorded using Bruker IFS 125 HR spectrometer at room temperature, at the spectral resolution of 0.01 cm⁻¹ and in a wide pressure range of H₂. The multispectrum fittings with the quadratic speed dependent Voigt profile were performed to retrieve the broadening parameters for H₂O spectral lines of 11 vibrational bands (2ν₁, 2ν₃, ν₁+ν₃, 2ν₂+ν₃, ν₁+2ν₂, ν₂+2ν₃, 2ν₁+ν₂, 3ν₂+ν₃, ν₁+3ν₂, ν₁+ν₂+ν₃ and 6ν₂).

The calculations of the broadening coefficients were performed in the framework of the semi-classical method with use of an effective vibrationally depended interaction potential [1]. The obtained broadening coefficients and literature data [2, 3] were used to determine the analytical dependence of some potential parameters on vibrational quantum numbers. The analytical expressions that reproduce the broadening coefficients for different vibrational bands are proposed.

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The use of spectral moments to simulate rototranslational collision-induced bandshapes

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Reliable knowledge of collision-induced absorption (CIA) is presently in demand for climate modeling. Traditional theories of CIA bandshapes [1] are inadequate to fully take into account intermolecular anisotropy, though this is indispensable provided polyatomic monomers are considered. Recent advances in quantum and classical theory (see e.g. refs. [2–4]) are impressive though extremely expensive as both human and computer resources are concerned. Irrespective to theoretical formalism chosen to simulate the spectrum the use of spectral moments is important to quantify dipole-forbidden absorbance. On the one hand, spectral moments are defined as integrals of the properly weighted binary absorption coefficient. On the other hand, the zeroth and second moments can be calculated directly via statistical average of either squared induced dipole or Poisson bracket composed of the dipole and Hamiltonian derivatives, respectively.

Current paper aims at rigorous derivation of classical expression for the second spectral moment followed by its use in the spectral absorption bandshape simulation. Several pair systems are considered as examples, such as CO₂–Ar, CH₄–Ar, N₂–H₂, CO₂–H₂. For each of these systems rigorous classical Hamiltonians are first derived assuming rigid monomers. Explicit *ab initio* potential energy and induced dipole surfaces for the above mentioned pairs are either newly calculated or borrowed from the literature. Then the zeroth and second moments of rototranslational CIA bands are calculated as functions of temperature. These theoretically found values are then compared with the experimental ones, which are available for a limited number of molecular pairs at some selected temperatures only. For heteromolecular systems the CIA profiles are simulated assuming that the CIA band can be represented as a sum of properly weighted CIA profiles for pure gases as was previously attempted in ref. [5]. The importance of spectrum desymmetrization procedure is demonstrated in order to take into account quantum effects when light hydrogen molecule is part of a pair under consideration. Special attention is paid to analysis of the CO₂–H₂ rototranslational band, for which first experimental data were recently obtained [6].

P1.43.

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The high resolution far infrared spectrum of ^{18}O enriched water vapor at the SOLEIL synchrotron

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The absorption spectrum of an highly ^{18}O enriched sample of water vapor is recorded by Fourier transform spectroscopy between 40 and 700 cm^{-1} at the AILES beam line using a standard radiation mode of the SOLEIL synchrotron. The ^{18}O enrichment of the sample was about 97% while pressure and pathlength values were 0.97 mbar and 151.75 m, respectively.

More than 5200 absorption lines were measured between 44 and 678 cm^{-1} . Among them, about 4500 water lines were assigned to more than 4800 transitions of seven isotopologues: H_2^{18}O , H_2^{17}O , H_2^{16}O , HD^{18}O , HD^{17}O , HD^{16}O , and D_2^{18}O . Numerous significant differences of line positions compared to those of the HITRAN2016 database [1] were found for the H_2^{17}O , H_2^{18}O , HD^{17}O , and HD^{18}O species. The maximum position deviation exceeds 0.15 cm^{-1} . The incomplete HITRAN's assignments of more than 90 transitions of H_2^{18}O and H_2^{17}O were finalized.

The lines of more than 2550 transitions of seven most abundant isotopologues were observed for the first time ($\text{H}_2^{16}\text{O} - 30$, $\text{H}_2^{17}\text{O} - 322$, $\text{H}_2^{18}\text{O} - 772$, $\text{HD}^{16}\text{O} - 130$, $\text{HD}^{17}\text{O} - 331$, $\text{HD}^{18}\text{O} - 931$, $\text{D}_2^{18}\text{O} - 28$). In particular, 28 new lines of D_2^{18}O were found in addition to the only study in this region [2]. The measured line positions will allow to refine and complete sets of the ground and first vibrational levels of H_2^{18}O and H_2^{17}O [3], HD^{18}O and HD^{17}O [4] and D_2^{18}O [5].

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Global depetrubation treatment of $5^1\Sigma_u^+$ and $5^1\Pi_u$ states in Rb_2

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New experimental data in the region $27\,000 - 29\,000\text{ cm}^{-1}$ enforced us to revisit the recently published analysis of the $5^1\Sigma_u^+$ and $5^1\Pi_u$ states in Rb_2 (Halalyova et. al JQSRT **202**, 328–334 2017). The new measurements, performed by polarization labeling spectroscopy not only significantly extended the range of experimental data to much higher vibrational levels of the $5^1\Pi_u$ state but also allowed us to identify transitions to two previously unobserved electronic states. The presence of both e and f parity levels and the analysis of the recent theoretical calculations (Allouche RA, private communication, 2017, Tomza M, private communication, 2017) suggested that these might be the $5^3\Pi_u$, $3^3\Delta_u$ or other triplet states, which become accessible from the singlet ground state through spin-orbit interactions.

Revealing the multiple structures of Glutamine

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Glutamine is α -amino acid that is used in the biosynthesis of proteins. The large flexibility of the molecule has several potential conformational candidates. Among them, the three most stable isomers have been characterized both using a laser ablation chirped pulse Fourier-transform microwave spectrometer (LA-CP-FTMW) and a laser ablation molecular-beam Fourier-transform microwave spectrometer (LA-MB-FTMW). Two of the conformers can be determined using the spectroscopic constants provided by the theoretical methods. On the other hand, the third conformer is not reproduced by conventional theoretical methods, and one should use some tricks to characterize the conformer's structure. Also, even the slightest different prediction in the site position of the nitrogen atoms makes the conformer's spectroscopic characterization very challenging because the nuclear quadrupole coupling interactions depend critically on the electronic environment, position and orientation of the ^{14}N nuclei. In this work, we highlight that more accurate theoretical methods are needed, and that glutamine can be used as a test to benchmark the calculations. We propose one trick to help the scientific community when the calculations are not sufficient to predict the structure and how to deal with the complex ^{14}N nuclear quadrupole hyperfine structure with no starting grounds.

Linear Rayleigh and Raman scattering to second order

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Both Rayleigh and Raman scattering are frequently used in spectroscopic measurements. The scattering can be described in terms of molecular polarisability tensors – with the resulting terms, arising from multipolar expansions of the scatterer's charge distribution, normally retained up to products of the electric-dipole electric-dipole polarisability with the electric-dipole magnetic-dipole/electric-dipole electric-quadrupole polarisabilities. In this work, we extend this usual multipolar theory of linear Rayleigh and Raman scattering to include the next-order correction.

The new terms promise a wealth of information about the shape of a scatterer, and yet are insensitive to the scatterer's chirality. Our extended theory might therefore prove especially useful for analysing samples in which the scatterers have non-trivial shapes but no chiral preference overall, as the zeroth-order theory offers little information about shape and the first-order correction is often quenched for such samples. A basic estimate suggests that our extended theory can be applied when the characteristic size of the scatterer is no more than approximately 1/50 of the incident wavelength. In this regime, the error resulting from neglect of the third- and higher-order corrections will be smaller than 0.1%.

Our results are entirely analytical, and apply to elastic light scattering in rarefied samples, and inelastic light scattering at essentially all sample densities – in both cases provided that the individual scatterers are independent, and multiple scattering is not important.

It remains to incorporate our results into more realistic, sample-specific theories, where the motions of the scatterers, local field corrections and other subtleties are taken into account. This is especially important for small scatterers and / or long wavelengths, as the second-order correction will be especially small in such cases.

The CRDS spectrum of natural and ^{13}C enriched carbon dioxide in the $1.73\text{ }\mu\text{m}$ window

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The CRDS spectra of natural and ^{13}C enriched carbon dioxide have been recorded by high sensitivity cavity ring down spectroscopy (CRDS) at room temperature in the $1.73\text{ }\mu\text{m}$ window ($5694 - 5879\text{ cm}^{-1}$) [1]. The investigated region corresponds to a transparency window of very weak opacity which is of particular interest for Venus.

A total of more than 1100 and 980 line positions and intensities were rovibrationally assigned to 26 and 22 bands in the natural and ^{13}C enriched carbon dioxide spectra, respectively, by the comparison with the accurate predictions provided by a global effective Hamiltonian and effective dipole moment operators. All identified bands belong to $\Delta P=8$ and 9 series of transitions, where $P=2V_1+V_2+3V_3$ is the polyad number (V_i being the vibrational quantum numbers). The weakest assigned lines have intensities on the order of $1\times 10^{-30}\text{ cm}^2/\text{molecule}$. Spectroscopic parameters were derived for the upper vibrational levels from a band-by-band fit of the line positions (typical *rms* values are on the order of $8\times 10^{-4}\text{ cm}^{-1}$).

Newly observed bands in the CRDS spectra of natural carbon dioxide include perturbed bands, weak hot bands and bands of minor isotopologues and provide critical validation tests for the most recent spectroscopic databases. The comparison to the Carbon Dioxide Spectroscopic Databank (CDSD), HITRAN2016 database and recent *ab initio* line lists is presented. Deficiencies are evidenced for some weak perpendicular bands of the HITRAN2016 list and identified as due to inaccurate CDSD intensities which were preferred to *ab initio* intensities. While Ames and UCL *ab initio* intensities are believed to be accurate within a few % for the strong unperturbed bands, the reported measurements allow evidencing important (>50%) differences between *ab initio* values of some weak perturbed bands.

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Rotational spectroscopy of organophosphorus chemical agents: Cresyl and Phenyl Saligenin Phosphate

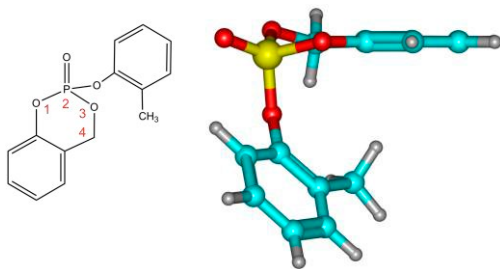
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Synthetic organophosphorous compounds (OPs) are used as pesticides, pharmaceuticals, additives or warfare agents, like the G- or V-series phosphonates. Microwave (MW) spectroscopy can be used for detection of these compounds based on its extreme frequency resolution and specificity, especially since the introduction of chirped-pulse excitation techniques allows for fast broadband operation. We have synthesized the neurotoxic organophosphates cresyl (CBDP) and phenyl (PSP) saligenin phosphate and characterized the molecules using cm-wave (2–8 GHz) chirped-pulse Fourier-transform microwave spectroscopy in a jet expansion. The molecules adopt a single conformation, with the six-membered dioxaphosphorinane ring adopting a P-O(3) half-chair configuration due to the introduction of a condensed benzene ring. In the two molecules, the oxygen double bond is equatorial, while the phenoxy group is axial to the dioxaphosphorinane ring. The introduction of a methyl group in the phenoxy group of CBDP (figure below) does not significantly change the orientation of the aromatic ring with respect to PSP. Rotational parameters and supporting ab initio/DFT calculations will be reported at the Conference.



FTIR laboratory measurement of O I spectra in the 0.77–12.5 μm spectral range: Rydberg states and oscillator strengths

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The normal system of O I terms available in the NIST Atomic Spectra Database was established more than a half-century ago and, in fact, reproduce the measurements performed by a Lund University group [1]. Although the accuracy of their wavenumbers was quite high, the accuracy of their level energies is critically dependent on the accuracy of the triplet 3s level. Moreover, for a better internal consistency of the system of transitions, it would be desirable to include the transitions between $n\ell$ levels with different $n = 3-8$, not only 3s, 3p and 3d. Some of these transitions lay in the wavelength range longer than 2 μm , which has never been measured in a laboratory with high resolution (except for two narrow bands studied in Ref.[2]).

The present work attempts to address the above issues. We exploit the great advantages of IR Fourier transform spectroscopy (FTS), such as its constant high resolution and energy throughput, to record high-resolution O I spectra in a wide range of 800–13000 cm^{-1} (0.77–12.5 μm). With the help of recent high-accuracy (0.004 cm^{-1}) direct measurements of the 3p level in the UV [3], we perform a reoptimization of O I level energies. Together with these UV lines and old line lists [1], we included high-resolution diode-laser measurements [2] and high precision fine structure splittings [3–4] into our reoptimization. This reoptimization also uses our own 135 O I lines in the infrared (including 51 lines not measured previously in the laboratory) to yield a consistent (within not worse than 0.01 cm^{-1}) system of O I levels with $n = 4-7$, $\ell \leq 6$. For some of these levels, we experimentally find fine structure splitting for the first time.

We also provide a long list of E1 line strengths, transition probabilities and oscillator strengths for O I IR transitions between high- ℓ states ($3 \leq \ell \leq 6$). These values are calculated with the help of quantum defect theory and show good agreement with the NIST values available for the transitions involving low- ℓ states ($\ell \leq 3$).

This work is funded by Czech Science Foundation (contract 13-07724S and grant 17-05076S), Russian Ministry of Education and Science (grants 3.4826.2017/8.9 and 3.1761.2017/4.6) and Russian Basic Research Foundation (project 16-32-0003)

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Structural determination of aroma molecules in the gas-phase

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High-resolution gas-phase studies allow for a fundamental understanding of molecular properties without any influences from the environment such as crystal fields or solvent effects. Therefore, understanding the molecular physics and intra-molecular properties of molecules can be extremely useful to fully elucidate changes during solvation (full- as well as stepwise micro-solvation) and molecular detection within complex environments such as the biological media. Here, we report and compare the structure and dynamic of several volatile molecules in the gas-phase [1]. Using a combination of molecular beam Fourier-transform microwave (MB-FTMW) spectroscopy and quantum chemical calculations we obtain highly accurate information of the conformational flexibility of our systems, which is used directly to validate quantum chemical calculations. Finally, we compare the energy differences of the most abundant conformers observed in the gas-phase in different implicit solvent models to compare their stability in various environments. The overall comparison of such aroma chemicals in different environments will help to push-forward the fields of molecular recognition, where until now, the prediction of molecular properties and biological activities remain underdeveloped and provide a great challenge.

High resolution study of the strongly interacting $\nu_3(\text{F}_2)/\nu_1(\text{A}_1)$ bands of $^{28}\text{SiD}_4$

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The high resolution infrared spectra of $^{28}\text{SiD}_4$ were measured in the 1500 – 1700 cm^{-1} region with a Bruker IFS 120HR Fourier transform spectrometer. The 1073 transitions with $J^{\text{max.}} = 42$ were assigned to the ν_3 band of $^{28}\text{SiD}_4$. Rotational, centrifugal distortion, tetrahedral splitting, and resonance interaction parameters for the (0010) and (1000) vibrational states were determined from the weighted fit of experimental line positions. The obtained set of parameters reproduces the initial experimental data with an accuracy close to experimental uncertainties. A further analysis of 150 experimental ro-vibrational lines was performed using the Hartmann-Tran profile to simulate the measured line shape and to determine experimental line intensities. The 3 effective dipole moment parameters were obtained on that basis from the weighted fit, which reproduce the initial experimental intensities of the 150 initial lines (both strong and weak) with the $d_{\text{rms}} = 7.5\%$. The half-widths of 50 ro-vibrational lines are analyzed from the multi-spectrum fit, and self-pressure broadening coefficients are determined.

Molecular spectroscopy using radio-acoustic detection and high power radiation in THz region

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Method of opto-acoustic (also called radio- or photo-acoustic) molecular spectroscopy is a powerful tool for both fundamental studies and applications. In this method the result of the interaction of the radiation with matter is detected by the change of the parameters of the matter and not of the radiation. It is likely the only method allowing reaching high sensitivity by increasing radiation power. This was particularly demonstrated in terahertz (THz) region in our recent work [1] using spectrometer with radio-acoustic detection of absorption (RAD spectrometer) [2] and radiation of a free-running gyrotron operating in continuous wave regime with up to 1 kW power [3].

In the reported study the gyrotron facilities were significantly improved for spectroscopic needs. In particular, the radiation frequency was stabilized against a reference oscillator using phase-lock loop (PLL) system in the anode voltage control [4]. The system provides high stability, narrow bandwidth (relative width about 10^{-12}) and accurate frequency control. Sample spectrum recording was possible at first (263 GHz), second (526 GHz) and third (789 GHz) harmonic of radiation frequency with modulation of both power and frequency. Typical spectra of different molecules obtained using the gyrotron and RAD method in different regimes of registration will be presented. Routine sensitivity of the spectrometer was demonstrated to be about $8 \times 10^{-10} \text{ cm}^{-1}$. Results were confirmed by high resolution spectra obtained using a BWO-based video spectrometer. Further perspectives of employing gyrotron for spectroscopy will be discussed.

The study was supported by Russian Science Foundation (project 17-19-01602).

Temperature dependence of collisional parameters of water 183-GHz line

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Water vapor line near 183 GHz is an important object for atmosphere remote sensing. This requires accurate spectroscopic information about line parameters, in particular, line intensity, pressure broadening and shifting, speed dependence coefficients and their temperature dependences.

Present study is devoted to measurement of temperature behavior of collisional parameters of the line. A BWO-based spectrometer with radio-acoustic detection of absorption [1] was employed. Main atmospheric species such as water and air (initially prepared as 78% of nitrogen, 21% of oxygen and 1% of argon) were chosen as buffer gases. Spectra were obtained at pressures from 0.01 Torr to 2 Torr in a wide temperature range from -25 to 85 C. Both Voigt and the quadratic Speed Dependent Voigt profiles were used for spectra analysis. Pressure broadening, shifting and their speed dependence were retrieved from the fit in wide temperature range. Temperature behavior of the measured parameters will be discussed. For the first time change of sign of self-shifting coefficient with increasing temperature was detected for this line. Obtained results may be useful for developing theory of molecular interactions, updating spectroscopic databases and for improving accuracy of radiation propagation models used for atmosphere remote sensing data analysis.

The study was partially supported by RFBR (grants No 18-02-00705, 18-05-00698).

Production of theoretical line lists for polyatomic molecules: SiH_4 , C_2H_4 , CH_3Cl , CH_3F , C_2H_2 , NH_3 , OH_3^+ , P_2H_2

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The ExoMol project aims to provide molecular line lists for exoplanets and other atmosphere with a particular emphasis on those atmospheres which are significantly hotter than the Earth's [1]. ExoMol has now computed line lists for about 50 molecules, many of which are polyatomics. The last ExoMol update included line list for following polyatomic molecules: SiH_4 [2], C_2H_4 [3], CH_3Cl [4] and CH_3F [5]. The line lists for C_2H_2 , NH_3 , OH_3^+ , P_2H_2 are close to be completed. The lists are produced using high level ab initio potential energy (PE) and dipole moment (DM) surfaces. For the variational calculations our programs DVR3D [6] and TROVE [7] are employed. The PE surfaces have to be refined by fitting to experimental data to reach the required quality. This contribution will discuss different important aspects of the production and storage of the hot molecular line lists. The high quality of our most recent line lists will be illustrated by comparing to the experimental data, including high temperature spectra.

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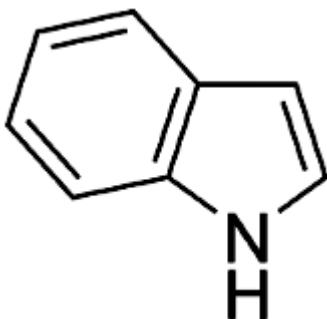
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Indole is a prototypical aromatic heterocycle molecule included in the human scent[1]. The rotational spectra of indole were investigated in 1988 in the frequency ranges of 9–12 GHz and 26.5–60 GHz[2]. In 1990, they were further studied in the frequency range of 18–40 GHz[3] and last year using FTMW spectroscopy in the frequency range of 7–19.5 GHz[4]. In these studies, the rotational and quartic centrifugal distortion constants of the ground and first vibrational states were obtained.

The present indole study was performed using the Prague millimeterwave spectrometer[5] in the frequency ranges of 140–160 GHz and 390–410 GHz. Hundreds of new rotational transitions were measured and assigned. A global fit of all the new and previously assigned transitions was performed by Pickett's SPFIT program[6]. The refined rotational and quartic distortion constants are presented and discussed.



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The visible spectrum of AID⁺: the experimental and theoretical treatment

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The emission spectrum of the AID⁺ ion has been studied by Fourier transform spectroscopy technique, as a further step of our investigation of the AID neutral molecule [1]. The 0-0 and 1-1 bands of the A²Π – X²Σ⁺ system have been recorded in the 27.000–29.000 cm⁻¹ region with an instrumental resolution of 0.03 cm⁻¹. In total, almost 500 rotational frequencies were measured with an absolute accuracy of about 0.005 cm⁻¹. It improved the experimental accuracy of the determined frequencies by the factor 10 compared to the previous work [2]. The rotational analysis has shown irregularities in the Λ-doubling splitting of the A²Π, v = 0, 1. Consequently, the A²Π state has been represented by the rotational term values, while the regular X²Σ⁺ state by the molecular constants. The causes of the irregularities were identified in the interaction between the A²Π state the lying higher the B²Σ⁺ state.

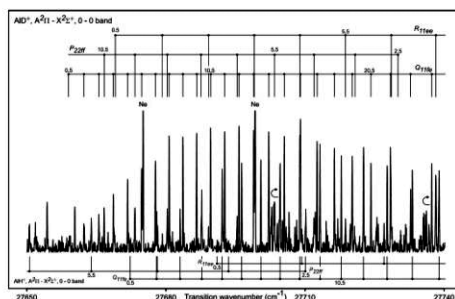


Fig.1. The VIS-FT emission spectrum of the AID⁺ A²Π – X²Σ⁺ (0-0) band.

Ab initio calculations on the ion were performed using a parallel version of the MOLPRO [3] (version 2010.1) suite of quantum chemistry codes. The static electron correlation was calculated using SA-CASSCF method [4]. The active space consisted of all the occupied valence orbitals of the aluminum atom plus the 1s orbital from the deuterium atom. The 1s orbital of the Al⁺ atom is kept frozen while the 2s2p orbitals are closed (kept doubly occupied in all configurations). In addition, SA-CASSCF can be used to calculate the excited electronic states corresponding to the Al⁺(³P)+D(²S) asymptote so a total of five states are included (2 × ²Σ⁺, ²Π, ⁴Σ⁺, ⁴Π). The accuracy of the potentials can be improved by including dynamic electron correlation, that was handled here by using MRCI method [5].

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High-resolution Fourier-transform spectroscopy of the comet-tail system in the $^{12}\text{C}^{17}\text{O}^+$ ion

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In the emission spectrum of $^{12}\text{C}^{17}\text{O}^+$ molecule new observations and analyses were performed. The (1,0) and (1,1) bands of the comet-tail ($\text{A}^2\Pi_i - \text{X}^2\Sigma^+$) system in the 18,900 to 22,100 cm^{-1} region were recorded with the Fourier-transform spectrometer (BRUKER IFS 125-HR). The absolute accuracy of wavenumbers was about 0.005 cm^{-1} . The measurement cycle included 128 scans within 1.5 h. As a source of the studied spectrum an air-cooled, carbon hollow-cathode (HC) lamp operated at 780 V, 54 mA dc was used. The lamp was filled with a static mixture of $^{17}\text{O}_2$ (70 %) and $^{16}\text{O}_2$ (30 %) at a pressure of about 1 Torr. During the discharge process, the O_2 molecules react with the ^{12}C atoms ejected from the carbon filler placed inside the cathode, thus forming $^{12}\text{C}^{17}\text{O}$ and $^{12}\text{C}^{17}\text{O}^+$ molecules in the gas phase, in amounts sufficient to finally achieve a signal-to-noise ratio (SNR) of 100:1 for the $^{12}\text{C}^{17}\text{O}^+$ ion. As a result of a detailed spectral analysis the individual molecular constants of both $\text{A}^2\Pi_i$ and $\text{X}^2\Sigma^+$ states were obtained. For the upper $\text{A}^2\Pi_i$ state all these constants were delivered for the first time. The parameters for the lower $\text{X}^2\Sigma^+$ state were also calculated and can be compared with these determined previously [1].

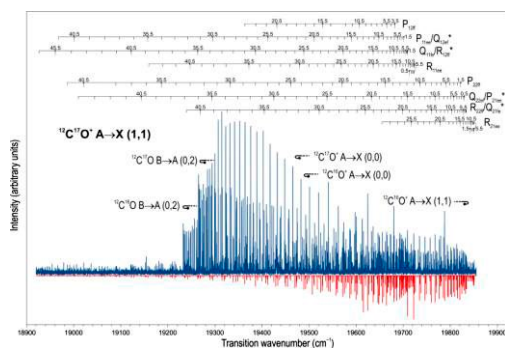


Fig. 1. High-resolution emission spectrum (upper trace) of the (1,1) band of the comet – tail ($\text{A}^2\Pi_i - \text{X}^2\Sigma^+$) system in the rare $^{12}\text{C}^{17}\text{O}^+$ isotopologue together with simulated spectrum [2] (lower trace) of this band. During analyses the influence of the other bands was taken into consideration: $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ B–A system (0,2) bands [3,4] as well as $^{12}\text{C}^{16}\text{O}^+$ and $^{12}\text{C}^{17}\text{O}^+$ A–X system (0,0) bands and $^{12}\text{C}^{16}\text{O}^+$ A–X system (1,1) band, simulated on the basis of constants from Ref. [5]. In case of $\text{P}_{11}/\text{Q}_{12}$, $\text{Q}_{11}/\text{R}_{12}$, $\text{Q}_{22}/\text{P}_{21}$ and $\text{R}_{22}/\text{Q}_{21}$ main/satellite branches (denoted by an asterisk) the values of the rotational quantum number J are provided just for the main branches.

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Self-broadening coefficients of rotational transitions of H_2S measured by submillimeter-wave spectroscopy

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Hydrogen sulfide (H_2S) is an asymmetric top molecule present in the atmosphere and that has been intensively studied by rotational and rovibrational spectroscopies [1]. It is a minor atmospheric pollutant produced by natural sources (volcanoes) and industrial processing of sulfur containing fossil fuels. Furthermore it is a byproduct of human activity such as water treatment processes. H_2S has also been observed in interstellar clouds in our galaxy (starburst galaxies) [2, 3].

However, as well as accurately measured and assigned line positions, pressure broadening coefficients are required for precise atmospheric monitoring and atmospheric column density determination. Rotational spectroscopy in the submillimeter domain has been chosen to determine self-broadening coefficients of H_2S from pure rotational transitions.

Using a frequency modulated computer-controlled spectrometer located at LPCA in Dunkerque [4], several ground-state rotational transitions of H_2S have been measured at room temperature in the region 168–865 GHz for pressures between 0.08 and 1 mbar. A non-linear least squares fitting of second harmonic spectra using the Voigt and speed-dependent Voigt profiles [5, 6] has been used to obtain the self-broadening coefficients of 32 lines ($0 \leq J'' \leq 11$, $0 \leq K_a'' \leq 7$). The observed J and K_a rotational dependences have been compared with values obtained by infrared and microwave measurements. No vibrational dependence of the self-broadening coefficients has been observed.

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Photodissociation dynamics of CF₂I₂ in solution

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Although chemical reaction dynamics of isolated molecules has been extensively explored and understood, that in liquid phase is much less comprehended due to the complication of solvent-solute interaction. One strategy to study reaction dynamics in solution is comparing solution-phase reactions with their gas-phase counterparts. The comparison helps us to explore which ideas from the study of gas phase reaction can be applied to that in solution [1]. Recent advances in ultrafast spectroscopic techniques make it possible to obtain a detailed information on the reaction dynamics in liquids. In particular, time-resolved infrared (IR) spectroscopy can probe transient molecular structures involved in chemical reaction pathways, providing critical information needed in solving the mechanisms of chemical reactions [2]. Here, photodissociation dynamics of CF₂I₂ in CCl₄ and c-C₆H₁₂ were probed by time-resolved IR spectroscopy in the time range from subpicosecond to microsecond. We were able to compose a complete photolysis dynamics of CF₂I₂ in solution including the fate of all the produced intermediates.

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Influence of the epigenetics marks in the non-covalent interactions between amino acids and DNA

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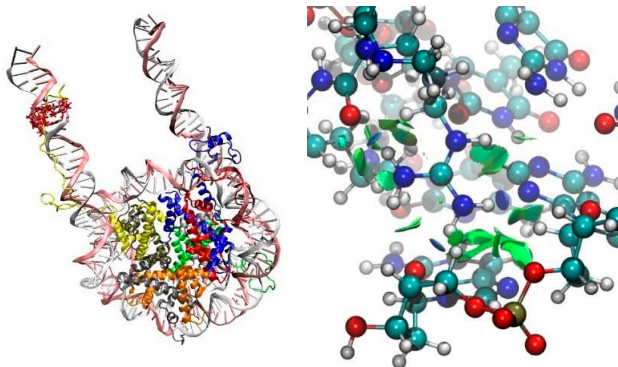
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The chromatin is a complex made by the DNA chain and proteins that, after an extremely efficient folding and packaging process, forms the chromosome in the nucleus of eukaryotic cells. Actually, the total length of all of the DNA in a human is around 300 times the Sun–Earth distance [1]. The basic repeating structural, and functional, unit of chromatin is the nucleosome. It has a disk shape that is stacked up in the packaging process to form the chromosome. This characteristic form is due to the quaternary structure of the proteins of the chromatin complex: the histones. Two of each of the H2A, H2B, H3, and H4 histones form an octamer, and about 146 base pairs bind and warp around the octamer in a 1.7 turns of DNA. The whole process is driven by non-covalent interactions, which enable easy unpacking whenever the DNA needs to be accessible for protein expression.

The DNA–histone interactions can be easily modulated, by placing methyl groups in the adequate sites of either the protein or the DNA strand. With this simple mechanism, it is possible to “silence” a gene and prevent it for being expressed into proteins. This modulation of the genomic machinery is known as Epigenetics and the methylation may even persist during reproduction, passing to the next generation.

In this work we built a realistic model [2], where the tripeptide H3A7–H3R8–H3K9 (Ala–Arg–Lys of the histone H3) interacts with a sequence of 3 DNA pair bases to see how the mono, di, and trimethylation of K9 affect the interaction of R8 with the minor groove of DNA, since these processes have been identified as transcriptional activation or repression depending on the number of the methyl fragments inserted. The structures of 4 models (252–261 atoms depending on the methylation state) have been optimized at PBE0–D3(BJ)/def2–TZVP level, using the COSMO approximation as implicit water solvent. The three dimensional NCI plots have been represented and analyzed to highlight the differences among the models and try to understand how the Lysine methylation process can facilitate or complicate DNA availability.



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Investigation on the degree of dissociation of Hydrogen plasma in PIG ion source via optical emission spectroscopy

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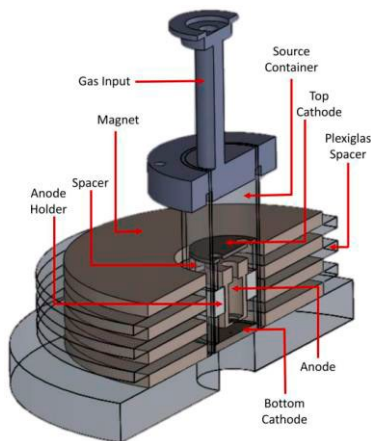
1) University Of Tehran

2) Institute for Research in Fundamental Sciences

Penning-type discharge plasma ion source is a powerful discharge device applied extensively in many fields [1]. Penning-type discharge ion source can work at the pressures below 1.33mbar and creates plasma with the electron temperature, higher than 5eV [2]. Our study perform at pressure and during the experiment it is constant.

Optical emission spectroscopy is easy and inexpensive methods for obtain important plasma parameters from spectral. We evaluated the electron temperature of the produced hydrogen plasma with Saha equation and the spectra lines emitted by neutral atomic hydrogen [3].

Main propose for this work is applying the spectroscopic method (OES[I]) for determination of the degree of dissociation of the hydrogen. For this aim we made PIG[II] with OES facility, Figure1.



[I] Optical Emission Spectroscopy

[II] Penning Ion Source

The method is based on the measurements of the relative intensities of two atomic lines of the Balmer series, H_{α} and H_{β} , and molecular line, (2-2) Q1 line of the Fulcher- α bands system and the method for determining the gas temperature is based on measured rotational distribution of intensity of Fulcher- α (2-2) Q bands of hydrogen, discuss in [4]. Finally, we extracted the degree of dissociation quantity from the electron temperature, gas temperature, Balmer and Fulcher intensities of plasma.

Key words: Electron temperature, Gas temperature, Penning ion source, Dissociation degree.

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The optimal origin for computation of wave functions of polar molecules

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It is commonly stated that the origin for the multipole expansion should be chosen in a way to minimize the magnitude of multipole term with the minimal l from the truncated ones [1,2]. This principle can allow to choose the optimal origin for computation of energy, but it can be shown that this origin is not universally optimal for computation of wave functions and related objects, like the probability density, dipole transition elements and oscillator strengths.

It can be shown, that the optimal location of the origin should be chosen in a way to minimize the distance to the most remote charge.

Fig. 1 shows that multipole computation gives quite high precision with the minimal number of multipole terms if the origin is optimally chosen (in the geometrical center of the system). The dipole-spherical function can be rather good approximation of the solution of Schrodinger equation if the origin is properly chosen.

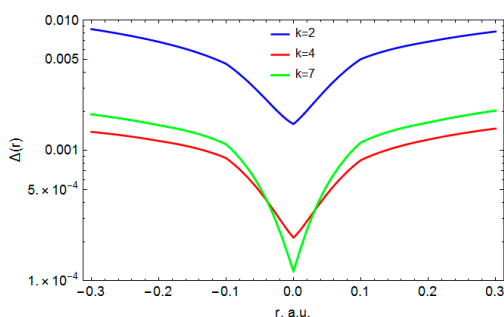


Fig. 1. The discrepancy between accurate solution of Schrodinger equation for three-center Coulomb potential and the solution for multipole expansion of the same potential as a function of origin location. k is the number of multipole terms used in expansion.

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The Rotational study of vitamin B6 form pyridoxine

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Vitamin B6, like the rest of vitamins, is an essential compound involved in numerous biological functions. Concretely, takes part in brain and nervous system health, in the metabolism of carbohydrates to produce energy and in the process of removing unwanted chemicals from our blood, among others. Vitamin B6 is found in a variety of forms, and here we present the rotational study of the pyridoxine form. Pyridoxine has been brought into gas-phase using laser ablation and probed by broadband LA-CP-FTMW microwave spectroscopy[1] in the range 2–8 GHz. The presence of a methyl group in the structure produces A, E doublets in the spectrum due to internal rotation that, together with the ¹⁴N quadrupole hyperfine structure, makes this study very challenging. The high resolution of LA-MB-FTMW[2] spectroscopy has been crucial to overcome this problematic.

Acknowledgments: The authors thank the financial fundings from Ministerio de Ciencia e Innovación (Consolider-Ingenio 2010 CSD2009-00038 program "ASTROMOL", CTQ2013-40717-P and CTQ2016-76393-P), Junta de Castilla y Leon (VA077U16) and European Research Council (FP/2007-2013) / ERC-2013- SyG NANOCOSMOS, are gratefully acknowledged. E. R. A. thanks Ministerio de Ciencia e Innovación for FPI grant (BES-2014-067776)

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Rotational spectrum of Methoxy Acetaldehyde: a combined CP-FTMW and millimeter wave study

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Methoxy acetaldehyde belongs to a group of structural isomers with general formula $C_3H_6O_2$ of which methyl acetate¹ and ethyl formate^[1–3] are known interstellar molecules. Two different high-resolution spectroscopic techniques have been used to provide direct experimental frequencies of methoxy acetaldehyde in a broad spectral range for astrophysical use. Jet-cooled broadband CP-FTMW spectroscopy between 6 and 18 GHz allowed the identification of the most stable *trans* form of methoxy acetaldehyde in the ground vibrational state and its singly substituted ^{13}C and ^{18}O isotopic species in natural abundances. Also, several water complexes were unveiled. The room-temperature millimeter-wave spectroscopy made possible to extend the assignment of the ground vibrational state up to 310 GHz and to identify five excited vibrational states of lowest-lying out-of-plane modes. Precise sets of spectroscopic constants presented here were used to search for the spectral features of methoxy acetaldehyde in the high-mass star-forming regions Orion KL and Sagittarius B2, as well as in the cold dark cloud Barnard 1. Upper limits to the column densities in these sources are given.

Acknowledgments: The authors thank the financial fundings from Ministerio de Ciencia e Innovación (Consolider-Ingenio 2010 CSD2009-00038 program “ASTROMOL”, CTQ2013-40717-P and CTQ2016-76393-P), Junta de Castilla y León (VA077U16) and European Research Council (FP/2007–2013) / ERC-2013– SyG NANOCOSMOS, are gratefully acknowledged. E. R. A. thanks Ministerio de Ciencia e Innovación for FPI grant (BES-2014-067776).

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Conformational study of Cyclooctanone using broadband rotational spectroscopy

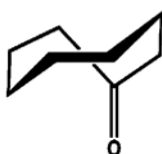
Ecaterina Burevski¹, Isabel Peña¹, Maria Eugenia Sanz¹

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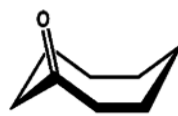
Cyclooctanone is an 8-membered ring ketone used as a precursor in the synthesis of more complex odorants and cyclic compounds, such as amber- and violet-smelling odorants, diesters of higher α,ω -dicarboxylic acids and 14-membered cyclic lactones. Being an 8-membered ring, cyclooctanone exhibits a complex conformational landscape. Cyclooctanone had been investigated using low resolution rotational spectroscopy, where only one conformer was observed.[1] However, the rotational constants were reported with high uncertainties of up to 100 MHz. We have reinvestigated the rotational spectrum of cyclooctanone using our 2–8 GHz chirped-pulse Fourier Transform Microwave (CP-FTMW) spectrometer.[2,3] In addition to the previously observed conformer, two other conformers have been identified in the rotational spectrum, and their rotational constants have been determined to high accuracy. The conformers adopt boat chair (BC) and twisted boat chair (TBC) configurations of the ring. The relative abundance ratios Cyclooct1: Cyclooct2: Cyclooct3 = 525:12:1 show that one of the boat chair conformers, the one first observed by rotational spectroscopy, is significantly more abundant than the others. The ^{13}C and ^{18}O isotopologues of cyclooct1 have been observed in their natural abundances, allowing determination of its effective and substitution structures.



Cyclooctanone 1 (BC)



Cyclooctanone 2 (TBC)



Cyclooctanone 3 (BC)

[1] T. C. Rounds and H. L. Strauss, *J. Chem. Phys.*, 1978, **69**, 268.

[2] D. Loru, M. M. Quesada-Moreno, J. R. Avilés-Moreno, N. Jarman, T. R. Huet, J. J. López-González and M. E. Sanz, *ChemPhysChem*, 2017, **18**, 268.

[3] D. Loru, M. A. Bermudez and M. E. Sanz, *J. Chem. Phys.*, 2016, **145**, 074311.

The monohydrate and dimer of Phenyl Ethyl Mercaptan by Rotational Spectroscopy

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The monohydrated cluster of phenyl ethyl mercaptan has been generated on a jet-cooled expansion and characterized using chirped-pulse Fourier transform microwave spectroscopy in the region 2–8 GHz. The monomer adopts two *gauche* and *trans* conformers, similar to phenyl ethyl alcohol but differing in the orientation of the *trans* thiol group. All monosubstituted (³⁴S and ¹³C) isotopologues could be measured for the *gauche* conformer. A single isomer of the complex of phenyl ethyl mercaptan with water has been identified. The heterodimer is stabilized primarily by the S–H...O hydrogen bond with water, assisted by secondary O–H... π interactions to the aromatic ring, while the homodimer of phenyl ethyl mercaptan (*g+g*–) is stabilized by a combination of S–H...S, C–H...S, S–H... π interactions to the aromatic ring. Supporting ab initio and DFT calculations will be presented.

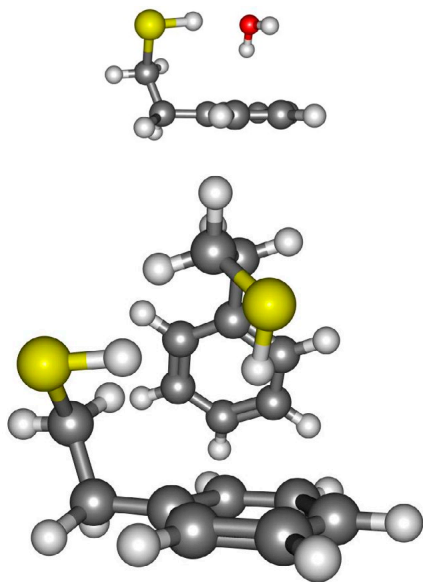


Figure 1. The monohydrate (left) and homodimer (right) of phenyl ethyl mercaptan.

Spectroscopy Group at the University of the Basque Country

Camilla Calabrese,^{1,2} Aran Insausti,^{1,2} Iciar Uriarte,^{1,2} Cristobal Pérez,^{1,2} Imanol Usabiaga,^{1,3} Maider Parra,¹ Francisco J. Basterretxea,¹ and Emilio J. Cocinero^{1,2}

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2) Biofisika Institute (CSIC, UPV/EHU), Universidad del País Vasco (UPV/EHU), Bilbao, Spain.

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The structural elucidation of molecular systems is a vastly explored aspect of science, as evidenced by the wide variety of techniques devoted to the task. In particular, high-resolution gas phase spectroscopy is able to unveil subtle structural and dynamical effects directly related to the chemical physical properties exhibited by a system, by isolating it from interactions with solvent or crystal packing. Moreover, by coupling these techniques with supersonic expansions, we can access the native conformational and aggregation preferences of molecules and intermolecular complexes.

The Spectroscopy Group at the University of the Basque Country (UPV/EHU) and the Biofisika Institute (CSIC-UPV/EHU) has built several microwave spectrometers. In our group, we have a chirped-pulsed FT-microwave spectrometer (CP-FTMW) equipped with a customized multi-valves system,[1] and a cavity based FT-MW spectrometer coupled with an UV ultrafast laser vaporization system.[2,3] Both set-ups are cutting-edge in the field of microwave spectroscopy. In addition, the Spectroscopy Group has strong collaborations with Prof. Corzana (Universidad de la Rioja), Dr. Çarçabal (Institut des Sciences Moléculaires d'Orsay) and Dr. Fernández (Universidad del País Vasco). These interdisciplinary collaborations allow us to investigate different biological and astrophysical topics since they grant us access to custom-made samples and various instrumentations and methodologies.

In order to illustrate our strategy, we present recent results focused on solving various structural problems of Chemistry at the molecular level. In particular, the conformational landscape of large clusters and biomolecules, including sugars, glycopeptides and drugs have been studied by our group recently.[3–6]

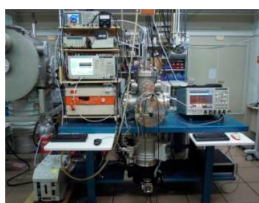


Figure. Microwave facilities available in Dr. Cocinero's Group at the University of the Basque Country (UPV/EHU).

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Nuclear spin conversion of ammonia isolated in noble gas matrices

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NH₃ includes three hydrogen nuclei and therefore has two nuclear spin isomers, ortho-NH₃ ($I = 3/2$) and para-NH₃ ($I = 1/2$), where I denotes the total nuclear spins of the protons. Elucidating the mechanism of the nuclear spin conversion (NSC) is important to correctly interpret the nuclear spin temperatures observed in comets such as Hale-Bopp and 153P/Ikeya-Zhang [1]. NSC is exceedingly slow in the isolated system but has been known to be accelerated in condensed systems [2,3]. Because the total wave function of a NH₃ molecule is required to be antisymmetric under the permutation of two protons, the nuclear spin states couple with specific rotational states. The rotational levels of NH₃ are labeled by the rotational quantum numbers of J and K . If K is (not) a multiple of 3, the nuclear spin isomer is ortho (para). In the present study, we investigated NSC of NH₃ in noble gas matrices by measuring time evolution of the infrared spectrum in the ν_2 -vibrational region.

The gaseous mixture of NH₃ and a noble gas was dosed onto a gold substrate at 9.5 K. The sample was warmed at 20 K for 3 min. After cooling to a liquid-helium temperature, infrared spectra were recorded at a resolution of 2.0 cm⁻¹ under an ultra-high vacuum.

Figure 1 displays time evolution of the infrared spectrum of NH₃ isolated in solid Kr in the ν_2 region. The assignments of the monomer peaks are described as follows : aQ(1,1)[p], 955 cm⁻¹ ; aR(0,0)[o], 973 cm⁻¹ ; sQ(1,1)[p], 979 cm⁻¹ ; aR(1,1)[p], 993 cm⁻¹ ; sR(1,1)[p], 1009 cm⁻¹. 'p' and 'o' in brackets mean that the corresponding peaks are due to para- and ortho-NH₃, respectively. An absorption peak of (NH₃)₂ was also observed at 998 cm⁻¹. The ortho peak increased in intensity with time whereas the para peaks decreased. This indicates that para-NH₃ converted to ortho-NH₃; the rotational relaxation from $J = 1$ to $J = 0$ occurred in connection with NSC. We plotted the integral intensity of aR(0,0) obtained by Gaussian fitting as a function of time. We determined NSC rates from the temporal changes of the integral intensity. The matrix- and temperature-dependence of the NSC rate will be discussed in the presentation.

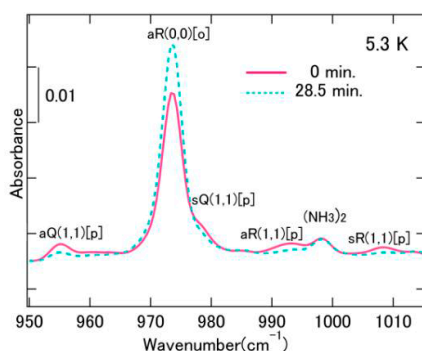


Fig. 1. Infrared spectra of NH₃ in solid Kr at 0 min and 28.5 min after the sample temperature reached 5.3 K.

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Simulation of rotational energy levels of the ground and first excited vibrational states of H₂S and SO₂ molecules using the effective Hamiltonian approach

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The ground (000) and first excited (010) are the key vibrational states of the H₂S and SO₂ molecules, as majority of the observed rotational – vibrational transitions in absorption originate from the rotational sublevels of these states. The experimental energy levels of the lower vibrational state are preferably used to determine the upper level of transition. However, the experimental rotational energy levels of the H₂S and SO₂ ground vibrational state were not available until recently [1,2].

In Refs. [1,2] a set of consistent experimental energy levels was derived from simultaneous consideration of the observed rovibrational transitions of H₂S and SO₂ molecules. The accuracy of the energy level determination in [1,2] depends on the accuracy of transitions involving this level, and in case of a lack of input data or their inconsistency, the resulted level may be considerably distorted. On the other hand, the set of experimental energy levels [1,2] is limited in J and Ka rotational quantum numbers. Then, an accurate simulation could support the energy levels values [1,2], or improve them by rejecting less accurate transition involved in level determination.

In this contribution an accurate set of calculated (000) and (010) rotational energy levels is obtained for the H₂S and SO₂ molecules from the fitting to the observed energy levels [1,2] using the effective rotational Hamiltonian based on different resummation methods of the divergent perturbation series. The predictive ability of the Hamiltonian's parameters derived is tested against variational calculations. Comparison of transitions wavenumbers obtained from the presently calculated set of the H₂S (010) energy levels with simulated (010)–(010) transitions included in HITRAN database revealed a large discrepancy.

This work is supported by the RFBR grant №18–02–00462.

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Analytical extension of hard-collision model of velocity-changing collisions in the Hartmann-Tran profile

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Daniel Lisak¹, Piotr Wcisło¹

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Recently recommended line-shape profile – the Hartmann-Tran profile (HTP) [1] includes all significant effects used in line-shape modelling nowadays [2]. Nevertheless, it gives unsatisfactory results in the analysis of high-resolution spectra with a prominent effect of

the Dicke narrowing [3], such as molecular hydrogen. Wcisło et al. [3] proposed a correction to the frequency of the velocity-changing collisions parameter in HTP corresponding to the Dicke narrowing effect. Although the correction works, it was applicable to the absorber to perturber mass ratio equals 1 and has efficiency only for the high ratio of frequency of velocity-changing collisions to the Doppler half width.

We propose the extension to this correction, making it useful not only in some specific cases, but for most of atmospheric and planetary spectroscopic applications. The correction enables to reproduce the molecular spectra with the percentage agreement to the more physically justified, but numerically complicated Speed Dependent Billiard-Ball line shape profile originated in the transport-relaxation equation [4] as shown in Figure 1.

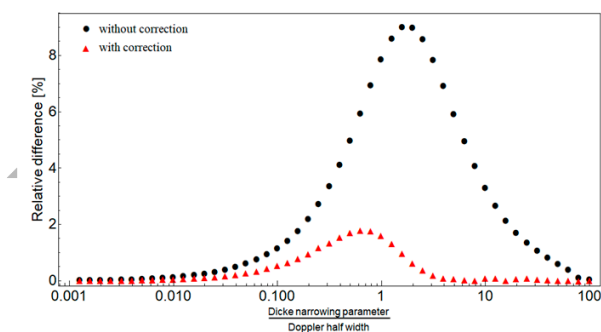


Figure 1. The relative difference between HTP without and with applied correction and the more advanced line-shape profile [3], dots and triangles respectively.

- [1] NH Ngo et al *J. Quant. Spectrosc. Radiat. Transf.* 2013 **129** 89–100.
- [2] J Tennyson et al *Pure Appl. Chem.* 2014 **86** 1931–1943.
- [3] P Wcisło et al *J. Quant. Spectrosc. Radiat. Transf.* 2016 **177** 75–91.
- [4] R Ciuryło et al *Phys. Rev. A* 2002 **65** 012502.

Far- and mid-infrared spectroscopy of matrix-isolated clusters and matrix-sublimated ice of D₂O

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Spectroscopic investigations of water clusters are important for understanding the nature of hydrogen bonding and have been intensively performed in the mid-infrared (IR) region [1]. On the other hand, in the far-IR region corresponding to the intermolecular vibration, only a few spectroscopic studies have been reported, and the spectral assignment has not been established yet. By using transmission electron microscopy and mid-IR spectroscopy, it has recently been reported that the structure of the ice obtained after sublimation of a matrix trapping water clusters is different from that of the vapor-deposited ice [2,3]. In the present study, far- and mid-IR absorption spectra of matrix-isolated clusters and matrix-sublimated ice of D₂O were investigated, using an apparatus for spectroscopy in the range of 50–7000 cm⁻¹ under an ultrahigh vacuum.

Our experimental apparatus consists of a Fourier-transform infrared spectrometer, a sample chamber, two optical boxes, and a detector compartment (Fig. 1). Each optical box and the sample chamber were separated by a diamond window, which is highly transparent to infrared and visible light. For the purpose of reducing the amounts of leak at the windows and keeping an ultrahigh vacuum in the sample chamber, the spectrometer, optical boxes, and detector compartment were evacuated with turbo molecular pumps. We switched between a HgCdTe detector (> 650 cm⁻¹) and a Si bolometer (< 650 cm⁻¹) by rotating an off-axis parabolic mirror in a high vacuum.

Figure 2a shows the spectrum of D₂O-containing solid argon (Ar/D₂O=100) formed on a gold substrate at 7.7 K. Absorption peaks of the intermolecular vibrational modes in Fig. 2b were assigned based on both the frequencies calculated with Gaussian 09 and the size distribution of clusters estimated from the mid-IR spectrum (Fig. 2c), where assignment has already been established. By subliming only the matrix under various conditions of the D₂O-concentration and the sublimation temperature, we obtained both the crystalline and amorphous ices. In the session, we quantify the degree of crystallization from the spectrum in the far-IR region where it is easy to distinguish between the crystalline and amorphous structures [4], and discuss the crystallization conditions of matrix-sublimated ice.

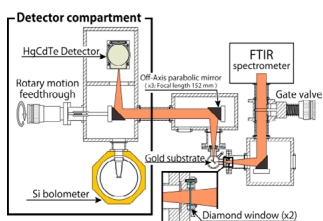


Fig.1 Experimental apparatus.

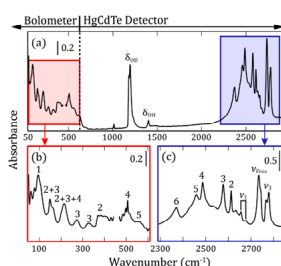


Fig.2 (a) Infrared spectrum of D₂O clusters in solid Ar at 7.7 K. Magnified views of the far- and mid-IR regions are given in (b) and (c), respectively.

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Laser absorption spectroscopy of $^{13}\text{CH}_4$ at 80 K and 296 K near $1.73\ \mu\text{m}$

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The absorption spectrum of $^{13}\text{CH}_4$ is recorded in the center of the tetradecad near $1.73\ \mu\text{m}$ ($5695\text{--}5850\ \text{cm}^{-1}$) at 296 K and 80 K by direct absorption spectroscopy (DAS) [1]. The achieved noise equivalent absorption of the spectra is $5 \times 10^{-8}\ \text{cm}^{-1}$ leading to line intensity detectivity threshold on the order of 10^{-25} and $10^{-26}\ \text{cm}^2/\text{molecule}$ at 296 K and 80 K, respectively. As a result two empirical line lists are constructed including about 3300 lines at room temperature and 2070 lines at liquid nitrogen temperature. For comparison, the HITRAN database provides in the region only the strongest $^{13}\text{CH}_4$ lines (about 440 lines in total). From the intensity ratios of the lines measured at the two temperatures, 1530 empirical values of the lower state energy level were derived (2T-method). Their accuracy is reflected by the clear propensity of the corresponding empirical values of the lower state rotational quantum number, J , to be close to integer values. They provide accurate temperature dependence for 91% and 99% of the total $^{13}\text{CH}_4$ absorption in the region at 296 K and 80 K, respectively. We revise some of incorrect J values included in HITRAN and compare our line list with the theoretical calculations [4] showing that the ab initio positions will have to be tuned according to our experimental values.

Acknowledgments

This work was performed in the frame of the Labex OSUG2020 (ANR10 LABEX56) and of the ANR project

e-PYTHEAS (ANR-16-CE31-0005). M. K. acknowledges the financial support of the French Government and the French Embassy in Poland.

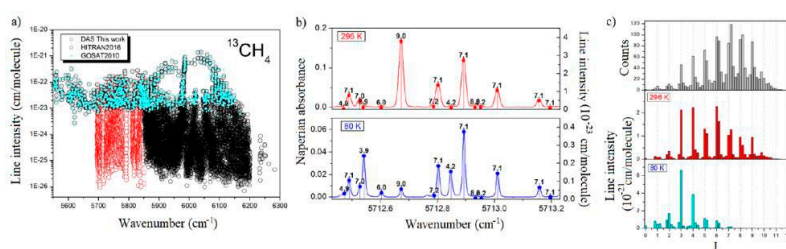


Fig. 1: a) Overview of the room temperature spectrum of $^{13}\text{CH}_4$ as provided by the HITRAN2016 database [3] (black open circles), the GOSAT2009 line list [5] and the present DAS data are plotted in light cyan and red, respectively. The HITRAN2016 line list in this region is formed by the GOSAT2009 list and the DAS line list of [6] below and above $5850\ \text{cm}^{-1}$, respectively. b) Example of empirical lower state J values derived by the 2T-method for transitions near $5713\ \text{cm}^{-1}$. c) Histograms of the empirical lower J values. Upper panel: Counts of the obtained J values with a step interval of 0.2. Medium and lower panels: Corresponding sum of line intensities at 296 K and 80 K.

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Nuclear spin conversion in matrix-isolated water monomer and dimer

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A water molecule is classified into either the ortho or para species, depending on its total nuclear spin. The abundance ratio of ortho to para, so called ortho-to-para ratio (OPR), has been measured for various interstellar media [1]. Recent experiments have shown that nuclear spin conversion (NSC) of a water molecule is rather fast in low-temperature condensed systems compared with the isolated system [2]. Therefore, the NSC mechanism needs to be revealed in order for the interpretation of observed OPR values. In addition, since water molecules tend to aggregate with each other to form clusters through the hydrogen bond, the experimental determination of the NSC rates in the water clusters is required for a further discussion of OPR. In the present study, we measured the NSC rates of the monomer and dimer of H₂O and D₂O isolated in rare gas matrices by using infrared spectroscopy.

All the experiments were performed in an ultrahigh vacuum. We mixed the gases of solute ($S = \text{H}_2\text{O}$, D_2O) and matrix ($M = \text{Ar}$, Kr , Xe) molecules in a gas handling system. The M/S ratio ranged from 200 to 10000. Each gaseous mixture was dosed onto a gold plate at a liquid-helium temperature. After annealing the condensate, we measured infrared spectra to monitor the rotational relaxation of S associated with NSC.

Figure 1 shows the time evolution of the infrared spectrum in the antisymmetric OD-stretching region at $\text{Kr}/\text{D}_2\text{O}=200$. The time when the substrate temperature settled at 7.1 K was set to be 0 s. Absorption peaks at 2753 (P1), 2774 (O), and 2787 cm^{-1} (P2) are assigned to the $0_{00} \leftarrow 1_{01}$, $1_{01} \leftarrow 0_{00}$, and $2_{02} \leftarrow 1_{01}$ rovibrational transitions of the D_2O monomer, respectively. While O corresponds to the transition of ortho D_2O , P1 and P2 originate from the para species. An absorption peak of $(\text{D}_2\text{O})_2$ also appeared at 2759 cm^{-1} . O grew with increasing time whereas P1 and P2 decayed. These temporal changes are attributed to NSC from para to ortho. From the time dependence of their integrated intensities, we determined the NSC rate of D_2O in solid Kr at 7.1 K to be $1.2 \times 10^{-2} \text{ s}^{-1}$. This rate was found to be one order of magnitude higher than that of H_2O . We also analysed the intensity change of a $(\text{D}_2\text{O})_2$ peak observed in the bending-vibrational region to estimate the rate of NSC in the dimer. We will discuss dependence of the NSC rate on the temperature, matrix species, H/D substitution, and clustering.

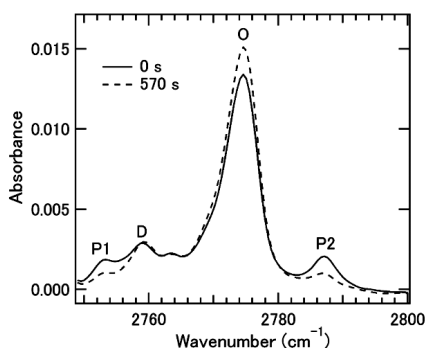


Figure 1 Infrared spectra of D_2O in solid Kr at 0 and 570 s. The substrate temperature was 7.1 K.

[1] M. J. Mumma et al., *Science*, 1986, **232**, 1523.

[2] R. Sliter et al., *J. Phys. Chem. A*, 2011, **115**, 9682.

Understanding metal compound chemistry in late-type star environments using chirped-pulse ft millimeter wave spectroscopy of supersonic jets

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¹) *University Kassel*

Modern telescopes like the ALMA (Atacama Large Millimeter Array) observatory in Chile, allow for a yet unprecedented view onto complex astronomical objects like late-type stars and their chemical environment. Dying stars eject huge amounts of their mass into outer space in form of gas and dust, thus being the major driver of cosmic chemical renewal. The formation of dust itself is yet not fully understood, especially the first condensation stages from atomic elements to di- and polyatomic molecules, like small silicate, aluminium, magnesium or titanium bearing oxides, carbides or nitrides (e.g. AlO₂, TiN/TiC, MgC). Currently many observed emission lines can not be assigned to the respective carriers due to a lack of high resolution laboratory spectra in the mm and submm range. To improve the situation and thus better exploit the capabilities of large facilities like ALMA, APEX, and IRAM30m, we started to set up a dedicated experiment in the 100 GHz region to investigate transient, mostly refractory materials (C, Si, metals, ...) bearing molecules. The set-up consists of a chirped-pulse Fourier transform millimeter spectrometer operating between 100 and 110 GHz using a high power radiation source of up to 1 Watt in combination with a laser ablation source producing a supersonic jet of buffer gas and the molecules to-be-investigated. First results will be presented.

Tropospheric reactions of triazoles with hydroxyl radicals

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1) LSAMA, University of Tunis el Manar

2) GSMA, University of Reims

We are interested in the theoretical study of the tautomeric equilibria of 1,2,3- and 1,2,4-triazoles and their reactions with hydroxyl radicals in the gas phase. All calculations were performed using the density functional theory (DFT/BHandHLYP) [1] with AVTZ basis set implemented in Gaussian 09.

A total of twenty-six chemical reactions has been studied, and thermodynamical data and rate constants are reported. The reactions can be classified in two categories: hydrogen abstraction and OH addition. Nine of these reactions are favourable at room temperature. It was found that OH addition proceeds more rapidly than hydrogen abstraction, by several orders of magnitude. For the most stable tautomers, which presumably dominate in the gas-phase, the fastest reactions are OH addition to 2H-1,2,3-triazole and site-specific OH addition to carbon atom 5 of 1H-1,2,4-triazole. In absolute values, however, the rate constants are rather small, $k = 5.82 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ and $k = 4.75 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$, respectively, at room temperature. Therefore, under the conditions of the troposphere, triazoles cannot be eliminated by reactions with hydroxyl radicals [2].

[1] Axel D. Becke. The Journal of Chemical Physics, 98(2):1372–1377, 1993.

[2] N. Derbel, O. Ferchichi, A. Alijah. Chem. Phys. Chem. (2018), DOI: 10.1002/cphc.201800049

Flexibility at the fringes: conformations of the steroid hormone β -estradiol

Sabrina Zinn^{1,2,3}, Melanie Schnell^{1,2,3}

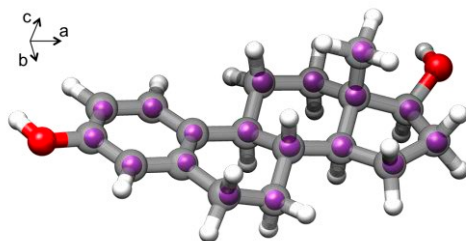
1) *Deutsches Elektronen-Synchrotron, DESY, Hamburg, Germany*

2) *Christian-Albrechts-Universität zu Kiel, Kiel, Germany*

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Estradiol, estrone and estriol are the three major forms of estrogenic hormones in women, which are responsible for the female reproductive system. Estradiol is the most physically active estrogen and is also widely used as medication, for example to prevent osteoporosis. The structure of estradiol features the rigid steroidal backbone ring system and two hydroxy groups at the fringes of the molecule that give rise to its conformational flexibility (Fig. 1). Along with a previous comparison of β -estradiol structures in the solid state and the liquid phase, this study completes the investigations in all three main phases by providing the interaction free gas-phase structure.

Here, we present a high-resolution rotational spectroscopy study of estradiol, employing the chirped-pulse microwave spectroscopy technique in the interaction free environment of the gas phase. It is the first rotationally resolved study of a steroid in the gas phase. β -Estradiol has a melting point of 177 °C and a molecular mass of 372 g/mol. Due to the high sensitivity and ongoing improvement of our experimental setup we were able to measure the spectrum of this large molecule and to determine its precise structure from the experimental data, as depicted in Fig. 1. Three conformers could be identified in the spectrum, which only differ in the orientation of the two hydroxy groups. The conformers are almost isoenergetic and have very similar rotational constants but still could be clearly resolved and assigned.



Franck–Condon simulated electronic spectra of gold carbene complexes

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Franck–Condon factor, the overlap integral between vibrational wave functions of initial and final electronic states, could find applications whenever electronic transitions are involved in the phenomena of interest. These include the original and familiar field of electronic spectroscopy: absorption and fluorescence, photoelectron spectrum, electronic sum frequency generation (SFG) spectroscopy, electron transfer, and nonradiative decay. Band shape or vibronic structure of electronic spectrum could be accounted for with the evaluation of Franck–Condon factors. Franck–Condon factor calculations have mainly applied in the electronic spectra of organic molecular systems; the investigations on metal complexes are very rare and attempts have not been made for gold complexes.

N–Heterocyclic carbene (NHC) chemistry has gained interest recently. Au(I)–NHC complexes, in particular, have received attention for strong Au(I)–CNHC bonds, their easy preparation and modification, and aurophilic attractions. Au(I)–NHC complexes often exhibit rich photoluminescence related to aurophilic interactions.

While aurophilic and argentophilic interactions are well known, gold(I) and silver(I) NHC complexes with heterometallic Au–Ag interactions are rare. Recently, crystal structures of {[Au(NHC)₂][AgBr₂]}1 and 2, of ester functionalized NHC, have been determined by I. J. B. Lin's group and show interesting photochemistry: the presence of an ester group in the NHCs not only induces mesophase formation but also promotes luminescent behavior of these heterometallic Au(I) NHCs. The N–substituted chain length could tune the emission wave length.

In this work, combined *ab initio* electronic structure and Franck–Condon factor calculations are carried out to simulate the band shape of electronic absorption and phosphorescence spectra of {[Au(NHC)₂][AgBr₂]}1 and 2 complexes.

FTIR measurements of the third overtone band of $^{12}\text{C}^{16}\text{O}$

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We report new data of the spectral line parameters in the ($4\leftarrow 0$) third vibrational overtone band of CO. The spectra of pure gas samples were recorded at 296 K, with a Bruker 125HR interferometer using 0.038 cm^{-1} spectral resolution. The pressures of CO were varied between 400 and 700 mbar. Due to the small intensity of the band, a multi-pass cell of 19.3 m optical path was used.

Intensities, line shifting and broadening coefficients are evaluated and will be reported together with the comparison to the available literature data [1].

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High resolution Ro-Vibrational analysis of C_2HD_3 in the region of 600 – 1150 cm^{-1}

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The present study is devoted to the analysis of the FTIR spectra of the C_2HD_3 molecule in the region of localization of the ν_{10} (A'), ν_7 (A''), ν_4 (A''), ν_8 (A''), ν_6 (A'), and ν_3 (A') fundamental bands. Earlier, [1], only the ν_8 fundamental band was investigated including Coriolis interactions between the ($\nu_8 = 1$) and ($\nu_6 = 1$) states. In this work an analysis of the ν_7 (A'') and ν_3 (A') fundamental bands was made for the first time.

The high resolution spectra of the C_2HD_3 molecule in the region of 600 – 1150 cm^{-1} have been recorded with a Bruker IFS-120 Fourier transform spectrometer at the Technische Universität Braunschweig (Germany).

Assignment of transitions was made on the basis of the Ground State Combination Differences method. Obtained on the basis of this information upper energy values were used as initial data in the weighted fit procedure of the Hamiltonian parameters. The obtained set of parameters reproduces the initial data with an accuracy close to experimental uncertainties.

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Fourier transform spectrum of $^{34}\text{SO}_2$ in the region of the ν_2 bending fundamental band

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High-resolution spectra of sulfur dioxide, $^{34}\text{S}^{16}\text{O}_2$, were recorded in the region of $400\text{--}650\text{ cm}^{-1}$ with a Bruker IFS 125HR Fourier transform interferometer (Zürich prototype ZP2001) equipped by a Ge: Cu detector.

Line strength and pressure broadening coefficients of the ν_2 and $2\nu_2\text{--}\nu_2$ bands were studied for the first time. Parameters of the effective dipole moment determined by the weighted fitting procedure allows one to reproduce experimental values with a $d_{\text{rms}} = 7\%$.

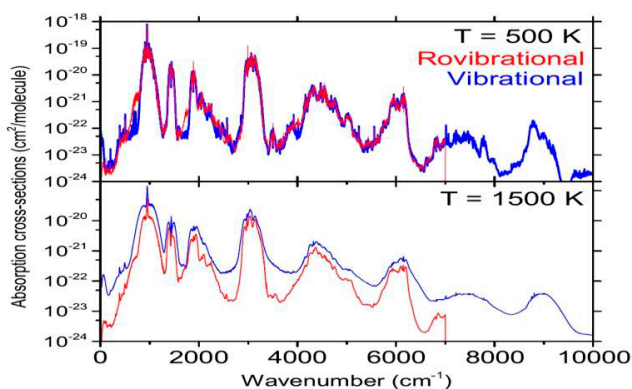
Realistic vibrational spectra of Ethylene Based on a 3-band model

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A technique for computing molecular opacities from vibrational band intensities is proposed and used to provide temperature dependent cross sections of ethylene for shorter wavelength and higher temperatures. When combined with realistic band profiles (such as the proposed three-band model), the vibrational intensity technique offers a cheap but reasonably accurate alternative to the full ro-vibrational calculations at high temperatures and should be better at retaining molecular opacities. Here we apply this model to the new line list of C_2H_4 [1] which is computed using TROVE [2] and based on high level ab initio potential energy and dipole moment surfaces. The line list covers the range up to 7000 cm^{-1} ($1.43\text{ }\mu\text{m}$) with all ro-vibrational transitions (50 billion) with the lower state below 5000 cm^{-1} included and thus should be applicable for temperatures up to 700 K . The 3-band model is constructed from three fundamental bands of C_2H_4 (one parallel and two perpendicular), which also represent its three dipole moment components. This $J=0$ -effort approach has allowed us to significantly extend the temperature as well as the frequency range of our line list and should be also useful for larger polyatomic molecules.



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Line positions and strengths in the ν_{10} / ν_7 bands of the C_2D_4 molecule

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The C_2D_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_2D_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.

High-accurate Fourier-transform infrared spectra of C_2D_4 were recorded and analyzed in the region of $460 - 850 \text{ cm}^{-1}$ where the strong fundamental bands ν_7 (B_{1u}) and ν_{10} (B_{2u}) are located. The spectra have been recorded with a Bruker IFS 120 Fourier transform infrared (FTIR) spectrometer (Braunschweig, Germany).

The assignment of the transitions was made on the basis of the Ground State Combination Differences method. In this case, the rotational energies of the ground vibrational state have been calculated with the parameters from [1]. All the obtained energy values were used then as input data in a weighted least square fit with the goal to determine rotational and centrifugal distortion parameters of the studied states of the C_2D_4 molecule. As the result, the set of fitted parameters reproduces the initial experimental energy levels with accuracy close to the experimental uncertainty.

A further analysis of experimental ro-vibrational lines of the ν_7 and ν_{10} bands of C_2D_4 was performed using the Hartmann-Tran [2] profile to simulate the measured line shape and to determine experimental line intensities. The effective dipole moment parameters were obtained on that basis from the weighted fit, which reproduce the initial experimental intensities with the $d_{\text{rms}} = 5.2 \%$.

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Direct deperturbation analysis of the L-mixed $B^1\Pi$ and $C^1\Sigma^+$ states of LiRb

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In recent years, ultracold alkali metal dimers have been found to have many promising implementations both in fundamental physics and quantum engineering. Amongst these are ultracold chemistry reactions, quantum information processing, and even the testing fundamental laws of physics. Li-containing heterodimers are particularly attractive candidates due to their high ground state dipole moment that makes it possible to manipulate them with external electric fields. However, to be able to utilize these molecules, one must first create a stable ensemble of ultracold molecules. One of the most widespread methods to accomplish this is the adiabatic transfer of ultracold Feshbach molecules from the lowest triplet electronic state to their absolute ground state ($v=0, J=0$). This transfer is a multistep process which *a priori* requires precise and comprehensive spectroscopic information on the involved electronic states.

In this work, we performed a direct deperturbation analysis of all experimental term values of the $B^1\Pi$ and $C^1\Sigma^+$ states that have recently become available in the literature for the $^{6,7}\text{Li}^{85,87}\text{Rb}$ isotopologues [1–4]. The rigorous coupled-channel modeling Hamiltonian accounts for the local L-uncoupling effect between the crossing $B^1\Pi$ and $C^1\Sigma^+$ states explicitly while the regular interactions with the remote states manifold are introduced into the Hamiltonian by the 2-nd order van Vleck's contact transformation. The initial set of the required interatomic potentials and L-uncoupling electronic matrix elements as a function of internuclear distance are obtained within the framework of high level *ab initio* electronic structure calculations [5]. The fitted non-adiabatic matrix elements and potential energy curves reproduce the overall experimental data of the interacting $B^1\Pi$ and $C^1\Sigma^+$ states with experimental accuracy (0.01 cm^{-1}). Particular attention is paid to the probe mass-invariant properties of the deperturbed structure parameters.

The study was funded by RFBR according to the bilateral Russia-Bulgaria research project 17-53-18006.

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High resolution study of the decades of H₂S

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High resolution spectra of the H₂S molecule in natural composition were studied in the region of 7300–8900 cm⁻¹ where transitions to the first and second decades are located. Line-by-line analysis, line strengths and self-broadening coefficients are obtained from the series of experimental recordings with the Bruker IFS 125HR Fourier transform interferometer (Zürich prototype ZP2001). Parameters of the effective Hamiltonian and effective dipole moment are obtained from the weighted fit procedure.

Absolute line strengths in bands ν_9 and ν_{11} of the $^{12}\text{C}_2\text{H}_4$ molecule

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High resolution analysis of the $^{12}\text{C}_2\text{H}_4$ spectra was made for the bands ν_9 and ν_{11} . The experimental spectrum in the region of 2900–3300 cm^{-1} was recorded with a Bruker IFS–120HR Fourier transform interferometer at Braunschweig, Germany.

More than 2 300 transitions with maximum values of quantum numbers $J^{\text{max}}=52$ and $K_a^{\text{max}}=13$ were assigned to the bands ν_9 , ν_{11} and $\nu_2+\nu_{12}$. The individual line intensities of about 300 transitions were determined from the fit of line shapes and then used in the weighted fit procedure for determination of the effective dipole moment parameters.

Analysis of resonance interactions in the bands located in the region of 1500–1750 cm⁻¹ in the C₂H₂D₂–cis molecule

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We report the result of a highly accurate ro-vibrational analysis of the C₂H₂D₂–cis molecule in the spectral region of 1500–1750 cm⁻¹. The FTIR spectra were recorded with a Bruker 120 HR spectrometer at the Technische Universität Braunschweig (Germany) under various conditions.

There are 6 bands (ν_2 , $\nu_7+\nu_8$, $\nu_4+\nu_{10}$, $2\nu_7$, $\nu_6+\nu_{10}$ and $\nu_4+\nu_8$) in this region. The $\nu_7+\nu_8$ band is strong, the other bands are relatively weak and they were not analysed before. For the $\nu_7+\nu_8$ band, transitions have been assigned with higher values of quantum numbers J_{\max} and K_a^{\max} than in the preceding work [1–2]. The states ($\nu_4=\nu_{10}=1$) and ($\nu_4=\nu_8=1$) were considered as “dark” states.

The ground state combination differences method was used for assignment of transitions. About 900 upper energy values obtained on that basis were used as an initial information in the weighted fit of parameters of the Hamiltonian, which takes into account resonance interactions between all considering vibrational states. The obtained set of parameters reproduce the initial data with an accuracy close to experimental uncertainties.

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High resolution study of $^{73}\text{GeH}_4$ in the dyad and pentade regions

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High resolution infrared spectra of $^{73}\text{GeH}_4$ were recorded at different pressures in the region of 650 – 2300 cm^{-1} with a Bruker IFS 120HR Fourier transform spectrometer (Nizhny Novgorod, Russia) and theoretically analyzed. More than 2500 transitions with $J^{\text{max}} = 22$ have been assigned to ν_2 / ν_4 bands of the dyad, and about 3000 transitions with $J^{\text{max}} = 30$ and 13 have been assigned to the stretching and bending bands of pentad. Line positions were used then in the fit of parameters of the corresponding effective Hamiltonians. Rotational, centrifugal distortion, tetrahedral splitting, and resonance interaction parameters were determined. Obtained set of parameters reproduces the initial experimental data with an accuracy closed to experimental uncertainties.

High resolution study of Hexades of H₂MS

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High-resolution infrared spectra of H₂S have been recorded in a wide region of 650–10400 cm⁻¹ with the Fourier transform interferometer Bruker IFS-125HR in Braunschweig Technical University.

The complete line-list of the studied bands of tree isotopologues, M=32, 33, 34, of hydrogen sulfide was produced including line strengths and self-broadening coefficients. Parameters of the effective Hamiltonian and dipole moment were obtained.

First high resolution analysis of SiD₄ in the dyad region

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The high resolution infrared spectra of SiD₄ were recorded with a Bruker IFS125 HR Fourier transform interferometer and analyzed in the region of 550–800 cm⁻¹ where the bands ν_4 and ν_2 are located. The 7279 transitions with $J^{\max.} = 37$ were assigned to the ν_4/ν_2 dyad (the ν_2 band is forbidden in absorption for symmetry reasons, and its transitions can appear in the spectrum only because of Coriolis interaction with the allowed ν_4 band). The subsequent weighted fit of experimentally assigned transitions was made with the Hamiltonian model which takes the resonance interactions between the (0001) and (0100) vibrational states into account. The initial values of the Hamiltonian parameters have been predicted on the basis of the isotopic substitution theory. As the result, a set of 35 fitted parameters was obtained which reproduces the initial 7279 ro-vibrational transitions with the $d_{\text{rms}} = 1.85 \times 10^{-4}$ cm⁻¹. A further analysis of about 600 experimental ro-vibrational lines in the dyad region of ²⁸SiD₄ was performed using the Hartmann–Tran line profile to simulate the measured line shape and to determine experimental line intensities. A set of 4 effective dipole moment parameters for the dyad of ²⁸SiD₄ was obtained on that basis from the weighted fit, which reproduce the initial experimental intensities of about 600 lines with the $d_{\text{rms}} = 6.5\%$. The half-widths of 40 ro-vibrational lines ($J^{\max.} = 16$) are studied from the multi-spectrum analysis, and self-pressure broadening coefficients are determined.

Ab initio calculations of the potential energy curves and intramolecular interactions in LiRb and LiCs including spin-dependent effects

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Ultracold molecules have recommended themselves to be convenient and interesting objects for experimental and theoretical investigations due to the ease of manipulation in laboratory environments. The first step towards making ultracold molecules is conducting a detailed study of the electronic structure of the molecule under examination.

In this work, a two-fold approach has been taken to accurately describe the potential energy curves (PECs) of the LiRb and LiCs heterodimers by looking at both (a) and (c) Hund's coupling cases.

For the latter case, the relativistic PECs of LiRb and LiCs, corresponding to the ground and low-lying excited dissociation limits, were obtained in a wide range of internuclear distances. The inner electronic shells of the Rb and Cs atoms were substituted with shape-consistent relativistic effective core pseudopotentials (ECPs) [1]. For the Li atom, an all-electron basis set [2], augmented by diffuse functions, was used. The energies of the electronic states were calculated using the recently formulated version of the intermediate Hamiltonian relativistic Fock-space coupled-cluster method with singles and doubles (IH FS RCCSD [3,4]). The $[\text{Li-M}]^{2+}$ ($M=\{\text{Rb}, \text{Cs}\}$) ion served as a vacuum state. The error, associated with the size-inconsistency of the applied method, was insignificant thanks to the dynamically shifted denominators.

As a result of the calculations performed for Hund's coupling case (a) non-relativistic PECs and non-adiabatic matrix elements were obtained in a wide range of internuclear distances. Small-core ECPs with 9 electrons (1 valence + 8 subvalence) for Rb and Cs, and a 1-electron ECP for Li were used within the framework of the internally contracted multi-reference configuration interaction (MRCI) method with state-averaged complete active space self-consistent field (SA-CASSCF) optimization, where core polarization effects were taken into account using *I*-independent core polarization potentials (CPPs).

The calculations were performed within the MOLPRO2010 and the appropriately modified DIRAC17 packages.

The study was funded by RFBR according to the research project N 18-33-00753.

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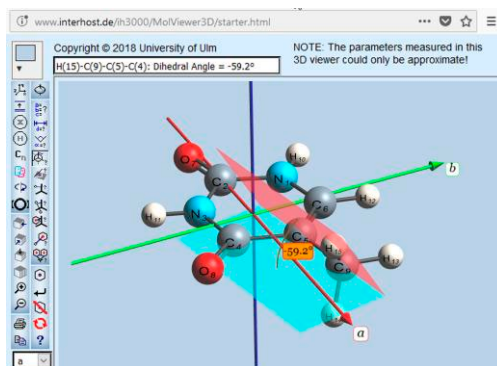
Comprehensive update of structural data in the MOGADOC database

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In order to facilitate the access to structural and structure-related properties of free molecules, our group has systematically compiled and critically evaluated the whole literature in the fields of microwave and high-resolution infrared spectroscopy, electron diffraction, and radio astronomy. On this basis the MOGADOC database (Molecular Gasphase Documentation) has been established [1–3]. In the meantime the database has grown up to 45,000 references and 12,000 inorganic, organic, and organometallic compounds. For 10,000 compounds the structural parameters such as bond lengths and internuclear distances, bond angles and dihedral angles are given numerically. The retrieval features of the HTML-based online-database have been described elsewhere [4–6]. More than 9,500 datasets can be visualized in three dimensions by a specially developed 3D-viewer [5]. In order to avoid problems with Java applets for the structure editor and 3D-viewer, we have recently replaced them by Java-scripts with enhanced features [6]. The implemented structure editor enables the user to retrieve structural formulas and their fragments. Moreover, one can interactively visualize the 3D-models and “measure” structural parameters by means of a 3D-viewer (see presentation of thymine from Ref. [7] in the figure), as well as analyze the symmetry of the molecule. In the next update, all structural data published up to 2017 will be presented in the database including bibliographical and key-word description.

This work has been supported by the Dr. Barbara Mez-Starck Foundation.



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A highly accurate *ab initio* dipole moment surface for water: transitions extending into the ultraviolet

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We present a new *ab initio* dipole moment surface (DMS) for the water molecule valid for transitions which stretch into the near ultraviolet. Intensities computed using this surface agree very well with precise laboratory measurements designed to aid atmospheric observations. This work is based on a data set encompassing 17 628 MRCI configurations that were calculated with the aug-cc-pCV6Z basis set with the Douglass-Kroll-Hess Hamiltonian to second order.

Compared to recent experimental measurements in the far infrared region[1], this new DMS significantly improves agreement with theory for transitions in the previously problematic bands (121), (300) and (102). For highly energetic overtones located in both the visible and ultraviolet regimes, we successfully predict the intensity of all measured bands to within 10% of the latest atmospheric observations[2]. These include bands at 487 nm (303), 471 nm (511), and 363 nm (900), for which previous models underestimated the intensity by up to 139%. Absorption features are also predicted in the 290 nm to 355 nm window and the theoretical shape demonstrates reasonably good behaviour with previously measured cross sections.

We will show the strong influence of the accuracy of the used fitted PES's to the accuracy of the intensities. For comparison a few different accurate PES's, one of them is the most accurate PES[3] up for now, were used.

P2.30.

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Far IR continuum absorption of H_2^{16}O and H_2^{18}O

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We present new measurements of the water vapor continuum absorption in the range covering most of the pure rotational spectrum of water molecule from 10 up to 650 cm^{-1} . The continuum absorption was derived from the broad band water vapor spectra recorded by Fourier transform spectrometer equipped with the 151-m multipass gas cell at the AILES beam line of the SOLEIL synchrotron. To cover the frequency range, the coherent ($10\text{--}35\text{ cm}^{-1}$) and standard ($40\text{--}700\text{ cm}^{-1}$) radiation modes of the synchrotron were used. In order to refine the magnitude and clarify the physical origin of the continuum, spectra of the two major water isotopologues, H_2^{16}O and H_2^{18}O , were considered. Recordings at several water vapor pressures were used to check the expected quadratic pressure dependence of the continuum.

The new data considerably extend and supplement results of previous measurements of the continuum filling, in particular, the gap between 200 and 350 cm^{-1} , which was never studied before. Investigation of the continuum absorption for both water isotopologues using coherent synchrotron mode confirmed existence of water dimer spectral feature near 15 cm^{-1} revealed in our previous study [1]. Improved signal to noise ratio will help to discriminate the contribution of stable water dimers and other sources of the continuum. The H_2^{16}O and H_2^{18}O absorption continua in the range of $50\text{--}650\text{ cm}^{-1}$ show similar frequency dependence and magnitude. The present data confirm that the MT-CKD empirical continuum model [2] widely used in atmospheric applications, overestimates the continuum magnitude by about 30% in the whole range of the rotational band of water molecule.

This work was partially supported by grant N° 18-02-00705 of Russian Foundation for Basic Research.

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A complete and coherent spectral line parameter set for the full $2\nu_3$ -band of $^{14}\text{N}_2^{16}\text{O}$ including line strengths, air- and self-induced broadening and shift coefficients

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We present a complete and coherent spectral line parameter set for the full $2\nu_3$ -band of the $^{14}\text{N}_2^{16}\text{O}$ isotopologue determined using high-resolution (0.002 cm^{-1}) FTIR-spectroscopy at 296 K between 1 and 1000 mbar. All line parameters were directly measured in the $2\nu_3$ -band with the same FTIR-infrastructure followed by analysis with the same software. The focus was put on metrological aspects. The latter includes traceability to the SI [1] of the most relevant input parameters, i. e. pressure, temperature and absorption path length, and determination of the respective uncertainties according to the GUM [2]. The data set consists of line strengths as well as air- and self-induced broadening and shift coefficients for the rovibrational transitions P40 to R40. In contrast to previously available line data for this spectral window in databases like HITRAN [3], for the first time, the complete $2\nu_3$ -band line parameter set was directly measured. The uncertainties of almost all parameters could be significantly reduced, e. g. in the case of line strengths and self-induced broadening and shift coefficients up to one order of magnitude for individual lines and all uncertainties are determined using metrological principles and rigorousness.

Considering the benefits of our results in comparison to previously often interpolated N₂O data, we suggest to evaluate the advantages of applying our coherent line parameter set as a potential new reference for atmospheric monitoring of N₂O, e. g. in the Total Carbon Column Observing Network [4]. The extension of our previous analysis [5] was realized within the continuation of the EUMETRISPEC project to establish a European spectroscopy infrastructure enabling measurements of spectral line parameters traceable to the SI.

P2.32.

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Rovibrational laser jet-cooled spectroscopy of the $\text{NH}_3\text{--Ar}$ complex in the ν_2 umbrella region of NH_3 : comparison between new infrared data and an *ab initio* calculated spectrum

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With our sensitive experimental set-up SPIRALES[1,2] which couples an external-cavity quantum cascade laser (EC-QCL) tunable between 930 and 990 cm^{-1} with a pulsed supersonic jet, we recorded in the spectral range near the ν_2 umbrella vibration 5 rovibrational transitions of the $\text{NH}_3\text{--Ar}$ van der Waals (vdW) complex (Fig. 1.a). The rovibrational analysis enabled the identification of the initial states of the observed transitions[3], namely an ortho state, $S_o(j=0, k=0)$, and two para states $S_p(j=1, k=1)$, $S_a(j=1, k=1)$. The final states of ortho transitions have been identified by rotational contour fitting and correspond to $P_{s/a, \text{lower}}(j=1, k=0)$ et $S_o(j=1, k=0)$. The comparison of the para transitions (Fig. 1.b) spectra with calculated spectra based on 4-dimensional potential energy surface that includes explicitly its dependence on the umbrella motion [4], enabled the assignment of the para transitions and the validation of the model used for the computation. The analysis of the para transitions excited state $P_{s/a, \text{lower}}(j=1, k=1)$, $P_{s/a, \text{upper}}(j=1, k=1)$ et $P_{s/a, \text{upper}}(j=1, k=1)$ [3], which label correspond to the major state contribution, has evidenced the existence of Coriolis coupling in fundamental and excited states, responsible of the unequal spacings in the rovibrational branches, and the frequency splitting of the *upper* of the inversion mode as a consequence of the coupling with Δ states.

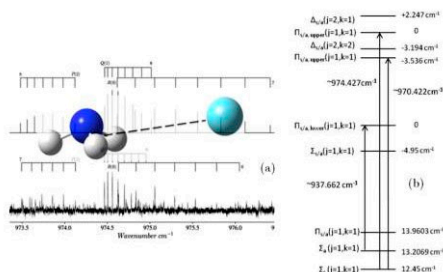


Figure 1. (a) Spectrum at 3K of $S_o(j=1, k=1) \rightarrow P_{s/a, \text{upper}}(j=1, k=1)$ transition calculated (up), experimental (down). Back projection: Equilibrium geometry of $\text{NH}_3\text{--Ar}$ complex. (b) Energy diagram of the complex in the inversion mode region of the para states.

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Exploring interstellar chemical processes of polycyclic aromatic hydrocarbons using opposite sides of the electromagnetic spectrum

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P2.34.

Polycyclic aromatic hydrocarbons (PAHs) are assumed to be key players in interstellar chemistry. Understanding their role in interstellar photochemistry and physics can provide important insights into the structure and evolution of the interstellar medium [1,2]. Thus, the combination of ultrafast experiments using highly ionizing radiation, along with the experimental structural investigation of PAHs and their intermolecular interactions with water using microwave spectroscopy, can help elucidate this role by providing complementary information on important interstellar physical and chemical processes.

In this work, we present our results on the ultrafast fragmentation of phenanthrene, a three-ringed PAH. The molecules were ionized using extreme ultraviolet radiation at 30.3 nm provided by the free-electron laser at Hamburg, FLASH [3]. Their reaction dynamics in the femtosecond regime were probed using IR and visible laser pulses at 800 nm and 400 nm respectively. The goal of these experiments is to determine the lifetimes of the excited cationic PAHs following extreme ultraviolet excitation, and thereby make valuable contributions in identifying the preferred reaction pathways of these molecules in space. In parallel to these pathways, a structural investigation has been made of the complexes of phenanthrene with H₂O using the chirped pulse Fourier transform microwave spectrometer (CP-FTMW) COMPACT operating in the 2–8 GHz region. Through this, we have been able to analyze the intermolecular interactions of phenanthrene–H₂O and phenanthrene–(H₂O)₂ complexes.

We expect that a thorough analysis of these intermolecular interactions is the first step in understanding the formation of interstellar ice at a molecular level. This, along with photodissociation studies, should lead to a deeper understanding of photochemical processes of these molecules in space.

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Laser-based hydrogen chloride measurements for biogas and biomethane applications

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Hydrogen chloride (HCl) is an important impurity to be quantified in biogas and biomethane for quality control reasons. Because of the reactive nature of HCl, it is necessary to accurately measure HCl concentrations in biogas and biomethane that is injected into natural gas grids, to avoid corrosion of metal containers due to HCl reaction with moisture [1]. Laser absorption spectroscopy provides a unique option to develop highly sensitive and accurate sensors for HCl measurements in biogas and biomethane [2]. For laser spectroscopic measurements where spectral modelling is applied, accurate line strengths, collisional broadening and shifting coefficients are required to model the absorption profiles [3, 4].

Here, we present new results of CH₄ and N₂ collisional broadening and shift of the 3.6 μm P₁(6) line, necessary for HCl concentration measurements in biogas and biomethane. The measurements have been performed in the pressure range of 10 to 1000 hPa, using a new mid-infrared interband cascade laser (ICL)-based direct absorption spectrometer specially designed for HCl measurements. Additionally, we elaborate on our measurement method, addressing the traceability of the results to the international system of units (SI) and uncertainty evaluation following guide to the expression of uncertainty in measurement (GUM) principles [5]. We validate our measurement method, showing the agreement of the line data with our previous measurements and available literature results [6].

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Bimolecular absorption in dry atmospheric gases at millimeter waves: new experimental data and high accuracy modeling

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Weakness of bimolecular absorption in nitrogen and oxygen makes it difficult for studying. However, its contribution is significant in the upper atmosphere and its accurate modeling is important. Several measurements of the absorption in compressed nitrogen and oxygen are known. However, to the best of our knowledge the only experimental study of the dry air absorption at atmospheric conditions in the millimeter wavelength region can be found [1].

Here we present new experimental data on bimolecular absorption spectra of dry atmospheric gases in the frequency range 105–150 GHz. The experimental spectra were recorded in a wide temperature and pressure ranges using a resonator spectrometer [2]. Good coincidence of our results for dry nitrogen absorption with the corresponding results from work [1] was observed.

Disagreement of N₂ and dry air continuum absorption observed in [1] was interpreted. The modified far wing model of the 60 GHz oxygen band involving the coupling effect between the zero-frequency O₂ lines was applied to solve the problem [3].

Comparison of the experimental results with the absorption calculated using the Millimeter-wave Propagation Model [4] shows that the model underestimates slightly the dry air atmospheric absorption in the millimeter range. Therefore, the corresponding part of the model can be corrected.

This work was partly supported by the Russian Foundation for Basic Research, Project No. 18–05–00698.

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[2] IEEE T THz Sci Techn, 2018, submitted

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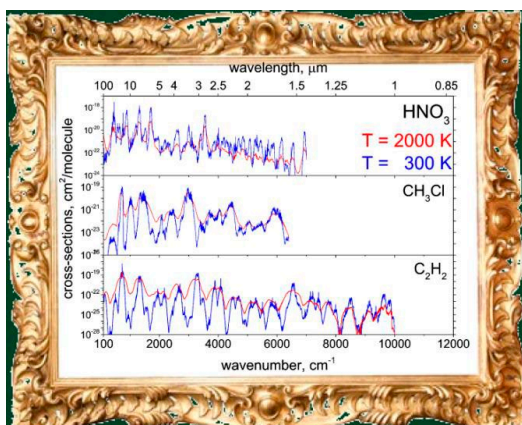
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Exoplanetary atlas of molecular opacities: ExoMol Gallery

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Molecular opacities play a key role for spectral characterization of atmospheres of exoplanets. These data form the input for opacity models for cool stars and brown dwarfs as well as for radiative transport models involving exoplanets. Different observational technics have different requirements on the quality of the spectroscopic data: some atmospheric studies need a complete description of molecular opacities, while other require very precise line positions. The ExoMol project is dedicated to providing molecular line lists for exoplanet and other hot atmospheres. So far ExoMol has generated line lists for about 30 key molecular species and more than 20 line lists have been collected from other sources. In 2017, ExoMol was updated with the line lists for NO [1], SiH [2], PO, PS [3], SH and NS [4], $^{17}\text{H}_2\text{O}$ and $^{18}\text{H}_2\text{O}$ [5]. The update from 2018 will include AlH [6], BeH [7], SiH₄ [8], H₂O [9], C₂, C₂H₂, C₂H₄, CH₃Cl, CH₃F, NH₃ and MgO. Here we present an exoplanetary atlas of molecular opacities produced using the ExoMol line lists in a form of a puzzle: we will suggest to recognize molecules by their spectra. Our spectral gallery is aimed at helping to identify prominent atmospheric absorbers based on their key spectral features. Methods for efficient production, storage and usage of line lists as well as further data needs will be discussed.



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1) VTT MIKES Metrology

Gas sensors based on optical absorption offer fast response, minimal drift, and high gas specificity with zero cross-response to other gases as long as their design is carefully considered. Furthermore, measurements can be made in real time and *in situ* without disturbing the gas sample. Thus, optical gas sensing fills an important gap between high-end laboratory equipment and low-cost sensors with inferior performances.

Figure 1 shows CO₂ absorption measured with an optical instrument. The blue dots correspond to experimental observations, while the black curve stands for a model function $\tau(\tilde{\nu})$ fitted to the experimental points. The model function $\tau(\tilde{\nu})$ assumes Voigt line shape, and optimal values for free parameters such as Lorentz widths and peak areas were determined with the help of a gradient-based minimization method along with the method of least squares. The red dots indicate the difference between observations and the fitted model function.

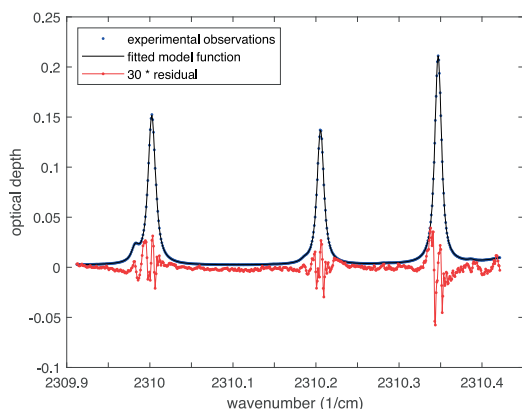


Figure 1: Results of a CO₂ absorption measurement and a model function $\tau(\tilde{\nu})$ fitted to the experimental points. The peaks at 2309.98 cm⁻¹, 2310.00 cm⁻¹, 2310.21 cm⁻¹ and 2310.35 cm⁻¹ correspond to isotopologues ¹⁶O¹²C¹⁷O, ¹⁶O¹²C¹⁶O, ¹⁶O¹²C¹⁸O and ¹⁶O¹³C¹⁶O, respectively. The red dots show the difference between observations and the fitted model function, and for illustrative purposes the difference has been multiplied by a factor of 30.

P2.38.

Isotopologue amount fractions can be calculated from the absorption peak areas, and we determine the peak areas by fitting our model function $\tau(\tilde{\nu})$ to the experimental points. However, we have noticed that gradient-based methods are very sensitive to the initial guess, because slightly different initial guesses may lead to C₁₃/C₁₂ ratios that differ by several per mil. Since an accuracy of 0.1‰ or better is sought, hundreds of spectra have to be measured to obtain the desired accuracy. Thus, a more robust fitting method would reduce the need for averaging and make the results generally more reliable.

A suitable fitting method has been developed in the context of positron annihilation lifetime spectroscopy[1]. First, a stochastic global optimization method called Simulated Annealing (SA) is used to pinpoint the approximate location of the global optimum. Subsequently, this point is used as an initial guess for a gradient-based minimization method. Finally, the solution space near the optimum is sampled with a Markov Chain Monte-Carlo Bayesian Inference (MCMC-BI) algorithm, which explores the distribution of solutions that are compatible with the experimental data. The use of SA and MCMC-BI makes the optimization computationally more demanding, but the solution is robust and independent of the initial guess. Based on this method, we will develop a fitting algorithm for mid-infrared spectra, and we believe that it will reduce the need for averaging and make the results generally more reliable.

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Nuclear spin conversion among three isomers in crystal II methane measured by infrared spectroscopy

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Methane containing four hydrogen nuclei exists in the form of three nuclear spin isomers: para ($I=0$), ortho ($I=1$), and meta ($I=2$). These isomers are related to the particular rotational states; para couples to $J=2$, ortho to $J=1$ and 2, and meta to $J=0$. Many investigations of nuclear spin conversion (NSC) in crystal II methane have been conducted [1, 2]. We previously reported that the rate of NSC between ortho and meta was 3 h^{-1} at 7 K. On the other hand, NSC between para and ortho/meta has been considered to be quite fast. Using the quantum relaxation model, Cacciani et al. roughly estimated that the rate of NSC from para to ortho was 250 s^{-1} at 4 K [3]. As far as we know, the time evolution of populations of three isomers has never been measured. In this study, we succeeded in observing NSC not only between ortho and meta but also between para and ortho/meta by infrared spectroscopy.

Our experimental apparatus is composed of an ultra-high vacuum chamber, an HgCdTe detector, and a Fourier transform infrared spectrometer. Gaseous CH_4 was introduced into the chamber and was condensed on a gold plate at 30 K. The sample was annealed at 38 K and was cooled down to 5.2 K. Each spectrum was measured at a resolution of 0.5 cm^{-1} with typically 18 scans accumulated.

The absorption spectra of crystal II methane showed rovibrational peaks after annealing (Fig. 1). The intensity of the $R(0)$ peak increased with increasing time. The intensities of the $P(1)$ and $R(1)$ peaks transiently increased in the first half hour and later decreased with time. In addition, the peak at 3018 cm^{-1} appeared just after cooling, which was assigned to the $Q(2)$ branch. The intensity of this peak significantly decreased with time. These temporal changes are attributed to the rotational relaxation associated with NSC among three isomers. Each integrated intensity as a function of time was determined by fitting the gaussian function and was analyzed using the double exponential function. As a result, we obtained two relaxation rates at 5.2 K: 0.48 h^{-1} and 2.3 h^{-1} . In this presentation, we demonstrate the detailed analysis based on the model of NSC among three isomers. Moreover, the validity of the previously-reported relaxation rates is discussed.

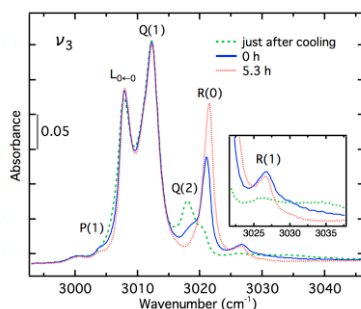


Fig. 1. Infrared spectra of crystal II CH_4 in the ν_3 vibrational region. The solid and dotted lines indicate spectra observed just after and 5.3 h after the sample temperature settled at 5.2 K, respectively.

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LED-based Fourier transform spectroscopy of HD¹⁶O and H₂¹⁶O in 14800–15500 cm⁻¹ spectral region

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The absorption spectra of natural and deuterium enriched water vapor are recorded in 14800–15500 cm⁻¹ spectral region with spectral resolution of 0.05 cm⁻¹ and optical pathlength of 3480 cm using a Fourier transform spectrometer with a LED as a light source. Detailed peaklists are constructed based on line profile modeling. Line positions are calibrated on wavenumbers reported in [1] for HD¹⁶O and in [2] for H₂¹⁶O. The accuracy of the resulted HD¹⁶O peaklist is estimated to be about 0.002 cm⁻¹ for positions of well resolved not-very-weak lines and 5–10% at best for intensities. The observed HD¹⁶O spectra are identified using experimental literature data and accurate variational calculation VTT [3]. In total, 879 HD¹⁶O lines are assigned, while only 467 lines in common with our data were previously reported in the region under study. About 90 new energy levels are determined, and 40 levels are corrected. For H₂¹⁶O in natural abundance 892 transitions are assigned.

Inconsistency on the order of 0.002 cm⁻¹ in positions of H₂¹⁶O lines recorded using a deuterated sample and those from natural water vapor spectrum is revealed provided that different calibration was applied for both spectra. Detailed comparison of presently recorded line intensities with the observed literature data and recent high-accuracy variational calculation [4] has shown that the calculated intensities may strongly deviate from their measured values for separate vibrational bands. Then, the data set obtained in this study will help to improve the quality of variational calculations of water vapor line intensities.

The work was supported by the RFBR grant N°16–43–700492/

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Collisional broadenings and shifts in the $S_0(0)$, $S_0(1)$ and $S_0(2)$ rotational lines of HD perturbed by He.

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Helium-perturbed HD is an important system for spectroscopic studies of the atmospheres of gas giants. For instance, a proper description of the collisional perturbation of the HD spectroscopic lines is needed for the accurate determination of the D/H mass ratio [1].

This work presents a comparison of the experimental and calculated values for the collisional line broadenings and shifts of the $S_0(0)$, $S_0(1)$ and $S_0(2)$ lines of the rotational Raman spectrum of HD perturbed by He at several temperatures between 77 and 300K. For the obtention of pure rotational Raman spectra we used a Stimulated Raman Spectroscopy setup previously described [2]. Since the frequencies of the pump and probe lasers are quite close, we worked with perpendicularly polarized beams and introduced additional polarization filtering elements instead of the usual frequency filters and dispersive optics. The experimental methodology consisted of systematic recordings of the spectral profiles of the HD lines in binary mixtures of the two gases at different partial pressures of He. HD pressure was kept approximately constant at 5 mbar for all scans, while perturber (He) pressure was varied between 50 and 500 mbar. The experimental line profiles were fitted to Voigt profiles allowing the removal of the well-known apparatus function and Doppler contribution, thus yielding the net collisional contribution to the profiles. A low pressure spectrum of pure HD was recorded between every mixture spectrum to provide a frequency calibration for the unavoidable wavemeters thermal drift allowing an accurate determination of the peak position variation as a function of the He partial pressure.

We performed the HD-He quantum-scattering calculations on a highly-accurate purely ab initio potential energy surface [3,4]. Taking advantage of the generalized Hess method [5,6] we used the scattering S-matrix to generate the parameters quantifying the collisional perturbations of the HD lines. Besides the usual shift and broadening parameters we determined the speed dependence of the broadening and shift as well as the complex frequency of the optical velocity-changing collisions.

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Terahertz spectra of Ambroxol

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This study presents the identification of polymorphs of Ambroxol hydrochloride using the terahertz spectroscopy. The spectrum of Ambroxol hydrochloride was measured from 5 to 80 cm⁻¹. The temperature dependence of the THz spectrum was studied in the range of 101 to 298 K. The measured spectra were analyzed and assigned according to the quantum chemistry calculations using the DFT/B3LYP with double zeta basis set. As determined by the QC calculations there are 12 vibration modes in the measured wavelength range. So far, 8 of them were assigned to the observed vibration bands.

Rotational spectra of 1,2,3,4-Tetrahydroquinoline

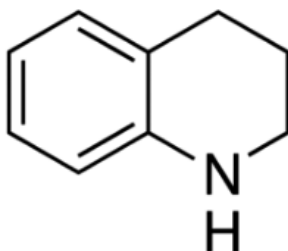
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1,2,3,4-tetrahydroquinoline is a partly saturated bioactive heterocyclic molecule[1] with low lying vibrational states contained in human scent[2]. Recently an analysis of the microwave spectrum in the frequency range of 7–20 GHz was published[3]. This study provided the prime rotational and quartic distortion constants of the ground vibrational state of the most stable conformer.

In the present study using the Prague millimeterwave spectrometer[4], rotational spectra were measured and assigned in the submillimeter ranges of 140–160 GHz and 390–410 GHz. More than 1300 new transitions were assigned. A global analysis of all the assigned transition frequencies involving all the new and previously measured transitions was performed by Pickett's SPFIT program[5]. The ground state refined rotational and quartic centrifugal distortion constants as well as the constants of the vibrationally excited states determined for the first time are presented in this contribution.

The presented study provides a list of the transition frequencies of an interesting heterocyclic molecule for astrophysical as well as human scent research. A comparison between the quantum-chemical calculations and the experimentally obtained constants of the vibrational satellites is also a notable part of this study.



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Evaluation of the current spectroscopic databases, such as GEISA–2015 and HITRAN–2016, in the frame of the preparation of the new release of GEISA

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The latest release of GEISA in 2015, including line parameters, cross-sections as well as aerosols, has been described in Jacquinet et al (JMS, 2016).

In parallel, the corresponding line parameters sub-database have been intensively validated using the powerful approach of the SPARTE chain (Armante et al, JMS, 2016) developed at LMD. For this release, important conclusions have been obtained, especially for H₂O, CO₂ and CH₄.

GEISA and associated management software facilities are implemented and freely accessible on the AERIS/ESPRI atmospheric data center website (<https://cds-espri.ipsl.upmc.fr/etherTypo/index.php?id=950\\&L=1>). It is used on-line in various domains like atmospheric physics, planetology, astronomy, astrophysic. Today, the GEISA database is the reference for current or planned TIR/NIR space missions, such as for IASI, IASI-NG, MERLIN, Microcarb.

We have now initiated the next release planned for the end of 2018, or the beginning of 2019. On this poster, we will present, first the current status of the spectroscopy, especially through the version 2015 and 2016 of respectively GEISA and HITRAN. In the second part, we will present a status of the molecule already updated in GEISA and what have been planned to finalize the 2018 version of GEISA.

High-resolution FTIR spectrum of SO₂ molecule between 2400 and 2650 cm⁻¹

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The experimental spectra in the region of 2400–2650 cm⁻¹ were recorded using Bruker IFS-120HR Fourier transform spectrometer with the spectral resolution of 0.0048 cm⁻¹ and wavenumber accuracy better than 10⁻⁴ cm⁻¹ for isolated not-very-weak lines. The spectrum was assigned based on the effective Hamiltonian calculations. In total, about 7000 transitions were identified for 101-000, 111-010, 121-020 vibrational bands of ³²S¹⁶O₂, as well as for 101-000 bands of ³³S¹⁶O₂ and ³⁴S¹⁶O₂. More than 1300 energy levels with rotational quantum numbers J as high as 89 and K_a as high as 24 were derived for the (101) vibrational state of the ³²S¹⁶O₂ molecule, while only 809 energy levels were recently reported in [1]. About 250 transitions were attributed to a very weak hot band 121-020 at 3520.139 cm⁻¹ observed for the first time. All experimental energy levels derived from the spectrum analysis were modeled using Watson-type effective Hamiltonian with the accuracy comparable with the experimental uncertainty. The spectrum assignment was confirmed by a comparison with the high accuracy variational calculations.

This work is partly supported by the RFBR grant №18-35-00575.

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Precision spectroscopy and global deperturbation analysis of the $A^1\Pi(v=0)$ state in $^{13}\text{C}^{18}\text{O}$

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We have reinvestigated the $A^1\Pi(v=0)$ level of $^{13}\text{C}^{18}\text{O}$ using new high-resolution spectra obtained via multi-photon laser excitation as well as with synchrotron-based Fourier-transform absorption spectroscopy of the $A^1\Pi - X^1\Sigma^+(0,0)$, $e^3\Sigma^- - X^1\Sigma^+(1,0)$, $d^3\Delta - X^1\Sigma^+(4,0)$, $a^3\Sigma^+ - X^1\Sigma^+(9,0)$, and $a^3\Pi - X^1\Sigma^+(11,0)$ bands. In addition, Fourier-transform emission spectroscopy in the visible range is performed on the $B^3\Sigma^- - A^1\Pi(0,0)$ band. Spectra of the $B^3\Sigma^- - X^1\Sigma^+(0,0)$ band are measured in order to tie information from the latter emission data to the level structure of $A^1\Pi(v=0)$. The high pressures in the absorption cell at the synchrotron and the high temperatures in the emission discharge permitted monitoring of high rotational quantum levels in $A^1\Pi(v=0)$ up to $J=43$. All information, in total over 900 spectral lines, was included in an effective-Hamiltonian analysis of the $A^1\Pi(v=0, J)$ levels that are directly perturbed by the $e^3\Sigma^-(v=1)$, $d^3\Delta(v=4)$, $a^3\Sigma^+(v=9)$, $D^1\Delta(v=0)$, $I^1\Sigma^-(v=0, 1)$ close-lying levels and the $e^3\Sigma^-(v=0, 2)$, $d^3\Delta(v=3, 5)$, $a^3\Sigma^+(v=8, 10)$ remote levels, as well being indirectly influenced by the $a^3\Pi(v=10, 11)$ state. This work is the next stage of the global project [2–7] of precise and comprehensive deperturbation analysis of the $A^1\Pi$ state in carbon monoxide using complementary spectroscopic techniques.

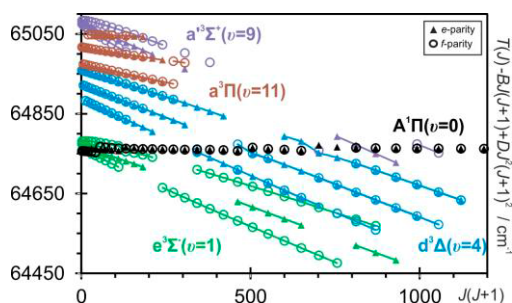


Fig. 1. Experimental reduced terms of the $^{13}\text{C}^{18}\text{O}$ $A^1\Pi(v=0)$ level and its perturbers.

[1] Corresponding author: hakalla@ur.edu.pl

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Precision FT spectroscopy and deperturbation analysis of the $A^1\Pi(v=0)$ state in $^{12}\text{C}^{17}\text{O}$

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- 4) School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85281, USA
- 5) Synchrotron SOLEIL, Orme de Merisiers, St. Aubin, BP 48, F–91192 Gif sur Yvette Cedex, France
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The present study focuses on a first analysis of spectroscopic data for the $A^1\Pi(v=0)$ level in $^{12}\text{C}^{17}\text{O}$. VIS–FT spectroscopy was used to obtain the Ångström ($B^1\Sigma^+ - A^1\Pi$) (0, 0) band spectrum under 0.018 cm^{-1} resolution. The discharge was conducted in the air-cooled, carbon hollow-cathode lamp. The temperature of dc-plasma at the centre of the cathode was about 1000 K. The estimated absolute calibration uncertainty (1σ) was 0.003 cm^{-1} . The fitting uncertainty of the line frequency measurements was estimated to be 0.005 cm^{-1} . The spectrum was combined with high-resolution photoabsorption measurements of the $^{12}\text{C}^{17}\text{O}$ $B^1\Sigma^+ - X^1\Sigma^+(0, 0)$ and $B^1\Sigma^+ - X^1\Sigma^+(0, 0)$ bands [2] recorded with an accuracy of 0.01 cm^{-1} using the VUV–FT spectrometer installed on the DESIRS beamline at the SOLEIL synchrotron. An effective Hamiltonian used in deperturbation analysis was performed up to $J = 39$, quantitatively addressing complex, multistate interactions with the $e^3\Sigma^-(v=1)$, $d^3\Delta(v=4)$, $a'^3\Sigma^+(v=9)$, $D^1\Delta(v=0)$, and $I^1\Sigma^-(v=0, 1)$ levels. The $A^1\Pi$ and perturber states were described in terms of a set of deperturbed molecular constants and perturbation parameters. This work is a member of a sequence of studies [3–7] analysing the $A^1\Pi(v=0)$ level in the CO isotopologues.

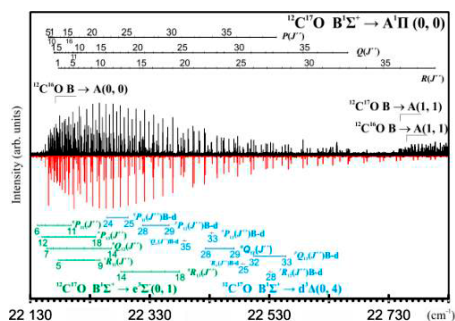


Fig. 1. Upper trace presents VIS–FT emission spectrum of the $^{12}\text{C}^{17}\text{O}$ $B^1\Sigma^+ - A^1\Pi(0, 0)$ band, as well as the $B^1\Sigma^+ - e^3\Sigma^-(0, 1)$ and $B^1\Sigma^+ - d^3\Delta(0, 4)$ extra-bands. Lower trace shows simulation of the $^{12}\text{C}^{17}\text{O}$ $B^1\Sigma^+ - A^1\Pi(0, 0)$ band.

- [1] Corresponding author: hakalla@ur.edu.pl
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Cavity ring-down spectroscopy of CH in the UV

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Pulsed cavity ring-down spectroscopy was used to measure rotationally resolved direct absorption spectra of the $C^2\Sigma^+-X^2\Pi$ electronic transition of the methyldyne (CH) radical. As the simplest carbon containing molecule it plays a vital role in the generation of complex organic molecules in the interstellar medium and is a significant part of stellar atmospheres. The spectroscopy of CH is also important in combustion chemistry where it is observed as the blue emission from hydrocarbon flames. Here, the CH radical was produced in a supersonically expanding planar plasma formed from a dilute mixture of acetylene in argon by means of a pulsed high voltage discharge source. The frequency doubled light of a pulsed dye laser was used to record spectra in the range of 305–330 nm.

Surprisingly the (0,0) (1,1) and (2,2) vibronic bands were all observed with similar intensities implying a high vibrational temperatures despite the cooling conditions in the supersonic expansion. Within each vibronic band rotational transitions from states with high rotational angular momenta were observed, implying rotational temperatures are also very high ($T_{\text{rot}} > 1000$ K). This high apparent rotational temperature facilitated the detection of previously unobserved transitions which resulted in improved rotational constants for at least the origin band. These results will be presented and the implications to plasma dynamics will be discussed.

THz Spectroscopy: a solution to monitor spoilage indicators. The case of Atlantic salmon

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Food spoilage is one of the most important challenges in today's world. In the industrialized countries, over 40 % of food losses produced annually have been estimated to be wasted at retail and consumer levels [1]. Spoilage of fresh food products is typically due to microbial activity. In general, seafood is highly susceptible to microbial spoilage.

Hydrogen sulfide (H_2S) is generated by many common spoilage bacteria [2]. Moreover, it has previously been used for monitoring the quality of muscle foods [3]. In this study we will demonstrate the feasibility of the THz technique for the monitoring of food spoilage. THz spectroscopy was used for measuring different H_2S levels in the headspace of Atlantic salmon (*Salmo salar*) packaged under 100 % N_2 .

Using a frequency modulated computer-controlled spectrometer [4], 10 samples of salmon fillets were measured at room temperature at 611.441 GHz. A non-linear least squares fitting of second harmonic spectra using a Voigt profile [5] was used to retrieve the H_2S concentration. The results were validated by comprehensive comparison with selective-ion flow-tube mass spectrometry (SIFT-MS).

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Structure and dynamics of substituted imidazoles in the gas phase

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Imidazoles are a class of aromatic *N*-heterocycles that exhibit versatile biological activity with some of their properties relating to anti-fungal, anti-bacterial and anti-HIV activity. Apart from its pharmacological importance, imidazole is the fundamental building block of many biologically important molecules such as adenine, guanine and histidine. The 5-membered ring contains two N atoms, pyrrolic and pyridinic, suggesting versatility in binding modes. The rotational spectrum of 2-methyl-4(5)-nitroimidazole was recorded in the 6–18 GHz frequency range with the aid of Chirped Pulse Fourier Transform Microwave (CP-FTMW) Spectroscopy employing supersonic expansion and laser ablation methods. The structure and binding properties of the molecule, as well as the methyl rotor dynamics, were investigated and experimental results are in good agreement with theoretical calculations using Density Functional Theory (DFT).

New spectral characterization of dimethylether isotopologues in the THz region

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Dimethyl-ether (DME) is a molecule found in star-forming regions, where it plays an important role in astrochemical processes [1]. Mono-deuterated DME [2] and singly substituted ¹³C-DME [3] have been detected as well. Despite this astrophysical interest, there is a lack of accurate spectral data of its isotopic species, which impedes further identification in the interstellar medium. The absorption spectrum of DME is quite dense and its analysis challenging because DME is an asymmetric top molecule with two internal rotors undergoing large amplitude motions. Thus, understanding such large amplitude internal motions on a quantitative level rely on quantum chemical models validated by laboratory data. However, one of the torsional bands is forbidden in the infrared spectra, that preventing the experimental determination of some of the interaction parameters.

We have recorded the Raman spectra of DME and of ¹³C-DME at room temperature, and of cooled DME in supersonic jet. We will introduce first the experimental approach [4, 5], and then we will present some Raman spectra of DME at different spectral regions. The spectral region of the torsional overtones of DME is rather complex due to their coupling with the C-O-C bending mode, and the presence of many hot bands. The spectrum of cooled DME allowed us to assign unequivocally the torsional overtones and their first hot bands, amending previous assignment from the literature [6]. In turn, the observed frequencies have been used to refine 3-D quantum calculations employing a torsion-torsion-bending Hamiltonian [7], along with an ab initio potential surface [8].

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Ab Initio potential energy surface and vibration–rotation energy levels of Germanium Dicarbide, GeC_2

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The accurate ground-state potential energy surface of germanium dicarbide, GeC_2 , has been determined from ab initio calculations using the coupled-cluster approach with the basis sets up to six-zeta quality. The core–electron correlation, higher–order valence–electron correlation, and scalar relativistic effects were taken into account. All of these effects appeared to be essential to achieve high accuracy. The potential energy surface of GeC_2 was shown to be extraordinarily flat near the T-shaped equilibrium configuration. The potential energy barrier to the linear CCGe configuration was predicted to be 1218 cm^{-1} . The vibration–rotation energy levels of some GeC_2 isotopologues were calculated using a variational method. The vibrational bending mode ν_3 was found to be highly anharmonic, with the fundamental wavenumber being only 58 cm^{-1} . Vibrational progressions due to this mode were predicted for the $\nu_1=1$, $\nu_2=1$, and $\nu_2=2$ states of GeC_2 .

The influence of water vapor isotopologues on the reflection coefficient of multilayer mirrors

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The influence of water vapor isotopologues (H_2^{16}O , H_2^{18}O and D_2O) on the reflection coefficient of multilayer mirrors was studied using a gas cell with multiple reflections from the mirrors. A strong change in the reflection coefficient of the mirrors (up to 0.9%) was found when water vapor under a pressure of 23 mbar was injected into the cell, which was interpreted as a change in the refraction index of the layers of multilayer coatings when water vapor penetrated into the porous coating structure. Gas-analyzer based on the CRDS spectrometer with dielectric mirrors with a reflection coefficient $R=0.9999$ was studied and the upper bound of the effect was estimated.

The work partly was supported by the Russian Foundation for Basic Research (Grants № 16-43-700492, 16-02-00802).

H_2^{16}O and H_2^{18}O absorption spectra between 16,460 and 17,200 cm^{-1}

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Two spectra of H_2^{16}O and H_2^{18}O vapor have been recorded between 16,460 and 17,200 cm^{-1} by Bruker IFS 125M Fourier-transform spectrometer at room temperature with spectral resolution of 0.05 cm^{-1} using high luminance LED light source and 60 cm multipath cell with a path length of 3480 cm. More than 1800 lines with minimum intensity value of 2.0×10^{-27} cm/molecule were observed in the spectrum of ^{18}O enriched vapor.

The comparison of recorded spectra against other observations [1] as well as with the simulations based on the HITRAN2016 database [2] and variational line list [3] will be presented.

About 1700 observed lines were assigned to more than 1800 transitions of H_2^{16}O , H_2^{18}O and H_2^{17}O water isotopologues. Assigned H_2^{18}O transitions allow us to obtain 422 rotation energy levels of 20 vibration states. The comparison of our energy set with the data reported by an IUPAC task group [4] is discussed.

The work partly was supported by the Russian Foundation for Basic Research (Grant № 16-43-700492).

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Monosulfur derivatives of methyl formate: millimeter and submillimeter wave spectra of S- and O-methyl thioformates

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S-methyl thioformate $\text{CH}_3\text{SC}(\text{O})\text{H}$ and O-methyl thioformate $\text{CH}_3\text{OC}(\text{S})\text{H}$, the sulfur derivatives of a rather abundant in the interstellar medium (ISM) methyl formate $\text{CH}_3\text{OC}(\text{O})\text{H}$ molecule, can be reasonably proposed as possible candidates for detection in the ISM. Both $\text{CH}_3\text{SC}(\text{O})\text{H}$ and $\text{CH}_3\text{OC}(\text{S})\text{H}$ exhibit complications in their spectra due to large amplitude methyl group internal rotation, although the internal rotation effect on the millimeter wave spectra is not the same for these two molecules because the barrier height to internal rotation is relatively low for the S- isomer ($V_3 \approx 130 \text{ cm}^{-1}$) and rather high for the O- isomer ($V_3 \approx 670 \text{ cm}^{-1}$). Previous experimental investigations were performed only for the S-methyl thioformate in the 10–41 GHz spectral range[1,2]. In this communication we present a recent progress achieved in the analysis of S- and O-methyl thioformate spectra in their ground and first excited torsional states. For the present study both methyl thioformate isomers were synthesized and the millimeter wave spectra were then recorded for the first time from 150 to 660 GHz with the Lille's spectrometer based on solid-state sources. The analysis of the spectra was performed using the Rho-axis method[3] and the fits within experimental error were achieved for both S- and O- methyl thioformates. In the presentation the details of this new study will be discussed.

Acknowledgements: Kharkiv group acknowledges the support of the Volkswagen foundation and the assistance of Science and Technology Center in Ukraine (STCU partner project #P686).

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Analyses of various ^{17}O and ^{18}O enriched isotopic species of ozone from FTS high resolution spectra

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This work continues the systematic investigation of high resolution infrared spectra of ^{17}O , ^{16}O and ^{18}O enriched isotopic species of ozone [1 and the references therein], recorded by the Reims Fourier Transform Spectrometer. Here we present the results of analyses of twelve bands of $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ in the 950–3850 cm^{-1} range. The fits are performed using the predicted values of rotational constants and resonance coupling terms from PES of ozone [2,3].

In addition, in a mixture of a total of 18 possible generated isotopic species of ozone two ν_3 bands are analyzed for the first time: those of $^{17}\text{O}^{17}\text{O}^{18}\text{O}$ and $^{17}\text{O}^{18}\text{O}^{17}\text{O}$ species, and four $\nu_1+\nu_3$ bands belonging to the $^{17}\text{O}_3$, $^{16}\text{O}^{17}\text{O}^{17}\text{O}$, $^{17}\text{O}^{16}\text{O}^{17}\text{O}$ and $^{17}\text{O}^{17}\text{O}^{18}\text{O}$ species.

The resulting sets of effective Hamiltonian parameters allow reproducing observed transitions within experimental accuracies and calculating synthetic spectra in excellent agreement with the observed ones. We also report here the comparison of main fitted parameters (band centers and rotational constants) with recent theoretical predictions [2,3].

P2.56.

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New version of S&MPO database on the ozone spectroscopy

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S&MPO is a web information system devoted to the spectroscopy of ozone. The original version has been developed since 2002 year and described in detail in reference [1]. We present here a new version, updated, with many improvements of scientific results and new graphical tools now available.

A. The main system has changed (architecture, implementation and user interface):

1. The application is completely rewritten, built now according MVC (Model–View–Controller) architectural pattern using modern tools as framework and javascript libraries.
2. New version of S&MPO has more advanced user interface.

B. The main scientific changes with respect to the old version are the following 3 points:

1. In addition to the previously available line lists corresponding to transitions computed from fitted parameters, another line lists are provided that includes observed line positions. This is important when the fit discrepancies due to local rovibrational resonances are experimentally significant.
2. Updated values of fundamental spectroscopic parameters with significant improvements with respect to line positions and intensities.
3. Addition of new isotopologues, particularly for oxygen–18 containing species as $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, and for oxygen–17 species, as $^{17}\text{O}_3$, $^{17}\text{O}^{17}\text{O}^{18}\text{O}$, $^{16}\text{O}^{17}\text{O}^{17}\text{O}$, $^{17}\text{O}^{16}\text{O}^{17}\text{O}$, $^{17}\text{O}^{18}\text{O}^{17}\text{O}$.

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Quantitative influence of the ozone potential energy surface upon dynamics of the $^{18}\text{O} + ^{32}\text{O}_2$ reaction

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We show, by performing exact time independent quantum molecular scattering calculations [1], that the quality of the ground electronic state global potential energy surface [2–3] and metastable ozone states [4] may be of utmost importance in accurately obtaining even as strongly averaged quantities as kinetic rate constants. The oxygen isotope exchange reaction, $^{18}\text{O} + ^{32}\text{O}_2$, related to the ^{18}O enriched ozone formation problem in the stratosphere, is explored in this context [5]. The thermal rate constant for this key reaction is now both in qualitative and quantitative agreement [6] with all experimental data available to date. A significant recent progress at the frontier of three research domains, advanced electronic structure calculations, ultra-sensitive spectroscopy, and quantum scattering calculations, has therefore permitted a breakthrough in the theoretical modeling of this crucial collision process from first principles.

P2.58.

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Analysis and theoretical modelling of the ^{18}O enriched carbon dioxide spectrum by CRDS near $1.74\ \mu\text{m}$

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The high sensitivity CRDS spectrum of a CO_2 sample highly enriched in ^{18}O is investigated in the $5702 - 5879\ \text{cm}^{-1}$ interval. The investigated spectral region corresponds to the $1.75\ \mu\text{m}$ transparency window of very weak opacity which is of particular interest for Venus. The recordings were performed at room temperature and pressure values of 1, 10 and 20 Torr. This work extends to lower wavenumbers the studies performed with the same sample in the $5850 - 7000\ \text{cm}^{-1}$ range [1–3] which provided a large amount of new spectroscopic information concerning the CO_2 minor isotopologues.

A total of 3210 lines belonging to 59 bands of nine carbon dioxide isotopologues ($^{12}\text{C}^{16}\text{O}_2$, $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$, $^{16}\text{O}^{13}\text{C}^{18}\text{O}$, $^{16}\text{O}^{13}\text{C}^{17}\text{O}$, $^{17}\text{O}^{12}\text{C}^{18}\text{O}$, $^{17}\text{O}^{13}\text{C}^{18}\text{O}$, $^{12}\text{C}^{18}\text{O}_2$ and $^{13}\text{C}^{18}\text{O}_2$) were rovibrationally assigned on the basis of the predictions of the effective Hamiltonian model. Among 59 assigned bands, 44 were observed for the first time. The accurate spectroscopic parameters of 53 bands are determined from standard band-by-band analysis (typical *rms* deviations of the line positions are $8 \times 10^{-4}\ \text{cm}^{-1}$). Three bands are found to be strongly perturbed by resonance first order Coriolis interaction. The new measured line intensities allowed determining or improving the $\Delta P = 8$ sets of the effective dipole moment (EDM) parameters for five non-symmetrical isotopologues – $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$, $^{16}\text{O}^{13}\text{C}^{18}\text{O}$, $^{16}\text{O}^{13}\text{C}^{17}\text{O}$, and $^{17}\text{O}^{12}\text{C}^{18}\text{O}$ – and $\Delta P = 9$ sets for the $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{18}\text{O}_2$ isotopologues ($P = 2V_1 + V_2 + 3V_3$ is the polyad number, V_i being the vibrational quantum numbers). The set of EDM parameters available for eleven isotopologues are used to discuss their isotopic dependence. The comparison to the Carbon Dioxide Spectroscopic Databank (CDS-296), HITRAN2016 database and *ab initio* Ames line list is presented.

This work is supported by the Laboratoire International Associé SAMIA between CNRS (France) and RAS (Russia, RFBR grant No. 16–55–16017) and by Tomsk State University Competitiveness Improvement Program. This work was performed in the frame of the Labex OSUG@2020 (ANR10 LABX56).

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Electronic structure of the molecular system $\text{HPS}^+/\text{HSP}^+$

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Astrophysical observations have shown that many molecules containing sulfur (SH , SH^+ , SN , SO^+ , SO_2 et OCS) were detected in the interstellar medium in significant density in different areas of the electromagnetic spectrum. Nevertheless, the molecular system HPS/HSP is not detected and the reasons for such non-detectability are not yet established. Recently, Ben Yaghlane and al [1] have characterized spectroscopically ground states of $\text{HPS}^q/\text{HSP}^q$ species ($q = -1, 0, +1$). Our work completes this study; it is to study the excited electronic states of $\text{HPS}^+/\text{HSP}^+$ system. One dimension potential cuts were calculated along the elongation as well as along the bending angle.

A global approach for deperturbation of NiH lowest-lying electronic states

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2) Institut Lumière Matière, Université Lyon 1 & CNRS

First-row transition metal mono-hydrides have been challenging to study because of their high multiplicities associated with numerous low-lying states. Some have been observed in spectra from sunspots and dwarf stars, where their response to magnetic fields can be used as probes for stellar magnetism. NiH is a priori one of the 'simpler' cases, with just one unpaired electron in its electronic ground state. Still, NiH has a complicated electronic structure and even the three lowest strongly spin-orbit-coupled electronic states are poorly studied. The currently existing data for these states cover only $v=0-4$ for the ground 2Δ state and $v=0-2$ for higher 2Σ and 2Π electronic states. Several attempts for analysis of these data have been made. The so-called supermultiplet model [1], which was extended later on [2,3], describes the ground and first two excited vibrational levels reasonably well, but it is based entirely on effective molecular constants.

An approach for global deperturbation of the close lying 2Σ , 2Π and 2Δ electronic states coupled by strong spin-orbit and rotational interactions will be presented. The present analysis is built on the same general physical assumptions for NiH electronic structure as in the supermultiplet model, but uses fully quantum mechanical coupled-channels method with potential energy curves and R -dependent coupling functions. NiD data are available [3] and should also be included in the current analysis.

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Dispersed fluorescence from NiD excited with a CW laser, taken in a novel way with a BOMEM DA3 interferometer

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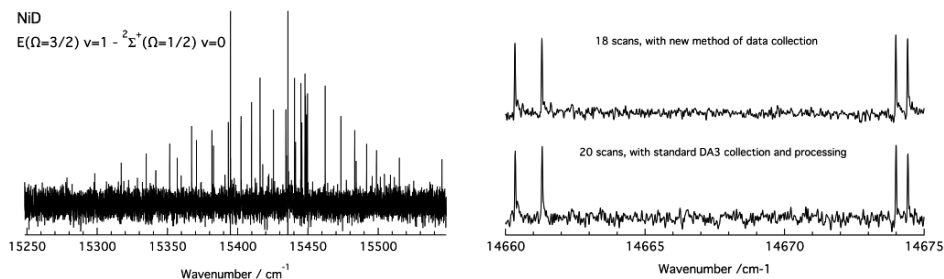
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While the spectrum of the metal hydride NiH has been extensively studied, spectra of the isotopologue NiD are much less extensive. Only 3 of the 5 strongly interacting molecular states arising from the d^9 ground-state configuration of Ni^+ have been reported, so modeling of these low-lying $^2\Delta_{5/2,3/2}$, $^2\Pi_{3/2,1/2}$ and $^2\Sigma^+_{1/2}$ states, including the strong spin-orbit interactions between them, is difficult. We report on experiments conducted in Lyon in which rotational levels of the $E(\Omega=3/2) v=1$ state of NiD produced in a hollow-cathode source are excited with a CW ring laser running with R6G dye (near 568 nm), following preliminary work in 2017 at the University of New Brunswick with a laser ablation molecular jet. Low-resolution dispersed fluorescence in the collision-free environment had shown emission where the $(1-0) E - ^2\Sigma^+_{1/2}$ band was expected, based on predictions[1]. Laser-induced fluorescence from $E(\Omega=3/2) v=1$ was recorded in Lyon with a BOMEM DA3 Fourier transform spectrometer at $\sim 0.04 \text{ cm}^{-1}$ resolution, locating not only rotational levels of $v=0$ in the $^2\Sigma^+_{1/2}$ state, but also in the (previously unreported) $v=0$ and $v=1$ levels of the $^2\Pi_{1/2}$ state.

We also discuss an alternative method for collecting the data using the DA3 spectrometer. The Lyon instrument dates from 1988, with an update to a PC interface in 1999. The processing power of the instrument is effectively limited by the memory of the PC, restricting interferograms to about 10^6 points. This calls for compromise between bandwidth and resolution in dispersed fluorescence spectra covering a wide wavenumber range. We have recorded interferograms, HeNe reference fringes and other signals available at various points on the instrument at high data rates (100–150 kHz) via a high-quality A/D conversion unit (Acces IO USB AIO-16-16E). The individual files, containing 5–15 scans at resolutions of 0.04 cm^{-1} , were very large (several hundreds of Mbytes) but sampled the signals about four times more frequently than the Nyquist criterion would require. The time axis of the data was then converted to an axis labeled in HeNe fringes using interpolation, and the interferogram was Fourier transformed and phase corrected to provide a spectrum that has a signal-to-noise ratio about twice what the DA3 software provides. This process allows us to obtain spectra of equal quality in one-fourth the time usually required. Others may be able to use our technique or a variant to revive similar Fourier transform spectrometers currently sitting idle.



Observation of a periodic many-body system

Klaus Muller-Dethlefs^{1,2}, Francois Michels²

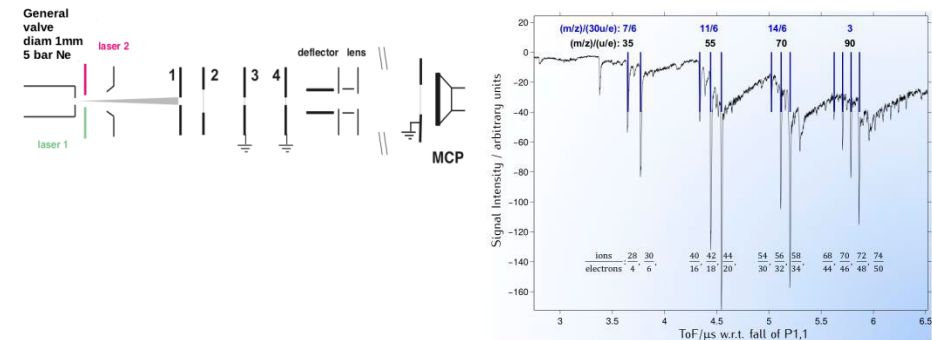
- 1) Xi'an Xiaotong University
- 2) The University of Manchester

We report the experimental observation of a very striking periodicity in a many-body system--an ultra-cold plasma. A long life-time (>0.3 ms) *quantum degenerate* molecular Rydberg plasma is generated in the high-density, high-collision rate region of a pulsed supersonic jet expansion by two-colour resonant excitation of nitric oxide (10%) in neon (5bar) into the high-*n*Rydberg threshold region close to the ionization limit. For plasma densities of $> 10^{16}\text{cm}^{-3}$ reached in our experiments the electrons should become quantum degenerate, i.e. the electron *de Broglie* wavelength becomes larger than the Wigner-Seitz radius *are*levant to describe the mean distance between the particles.

The time-of-flight (ToF) mass spectrometer used is depicted in the figure. Experimentally, two synchronous UV laser pulses produce the plasma a few mm away from the jet nozzle. After $170\mu\text{s}$, when the plasma cloud is still *ca.*130mm in front of aperture plate 1 (ap.1), two successive high-voltage (HV) pulses of 3.6 kV with a $0.2\mu\text{s}$ gap are applied to ap.1. The first HV pulse (P1,1; length $5.5\mu\text{s}$) is followed by a gap of $0.2\mu\text{s}$ and a second pulse: P1,2. The observed ToF spectrum w.r.t. the falling slope of P1,1 is shown in the figure (positive particle detection on MCP). The observed sharp peaks ("slices") in the ToF spectrum follow a fully reproducible progression of (*m/z*) mass to charge ratios from 35 to 92.5 (blue: w.r.t. *m*(NO⁺) = 30u). From the *m/z* ratio one obtains the corresponding ion to electron ratios of the 12 slices (denoted in the bottom of figure), from 7/1 to 37/25.

In conclusion, we observe a many-body system consisting of a series of objects that contain a magic number of ions and electrons for which the *ion/electron* ratio follows a periodicity (not or only weakly observed): **14/2, 15/3, (16/4, 17/5, 18/6, 19/7), 20/8, 21/9, 22/10, (23/11, 24/12, 25/13, 26/14), 27/15, 28/16, 29/17, (30/18, 31/19, 32/20, 33/21), 34/22, 35/23, 36/24, 37/25**. These objects are manipulated by electric fields in a ToF spectrometer without being destroyed, which shows that they behave as objects with a centre of mass. The observation of such many-body states with periodic ion/electron ratios suggests a phase correlation and possibly quantum entanglement. The path from *Structure and Phase to Quantum Entanglement* is of considerable interest in complex systems. Starting from the common textbook opinion that in many-electron atoms the electrons are quantum entangled (a deeper reason for the periodic system of the elements), one can speculate that the observation of periodicity in the many-body system presented here might originate from quantum entanglement.

As a perspective for molecular spectroscopy, such a plasma could provide a sympathetic cooling environment for larger molecular systems beyond existing methods.



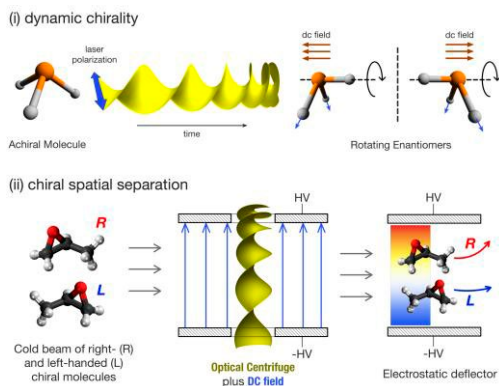
Creating, imaging, and controlling chiral molecules with electric fields

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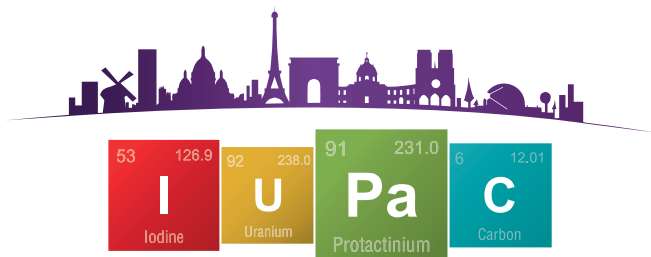
Chirality is now one of the top-class subjects in physical, chemical and biological academic research as well as industrial pharmacology. Accurate experimental characterisation of the enantiomeric excess and absolute handedness in mixtures of chiral molecules, efficient chiral purification and discrimination remain very challenging and highly demanding tasks for a broad scope of applications. A number of novel experiments have recently been developed for measuring the enantiomeric excess [1,2] and absolute handedness [3] as well as preparation of the enantiomerically enriched samples [4].

We will present few novel robust techniques using laser and static electric fields for (i) inducing dynamic chirality in statically achiral molecules [5], (ii) efficient spatial separation of chiral molecules, as well as (iii) detecting the enantiomeric excess [6]. The results are based on the robust and highly accurate variational simulations of molecular ro-vibrational dynamics in the presence of electric fields [7]. Challenges and perspectives for experimental realisations are discussed.



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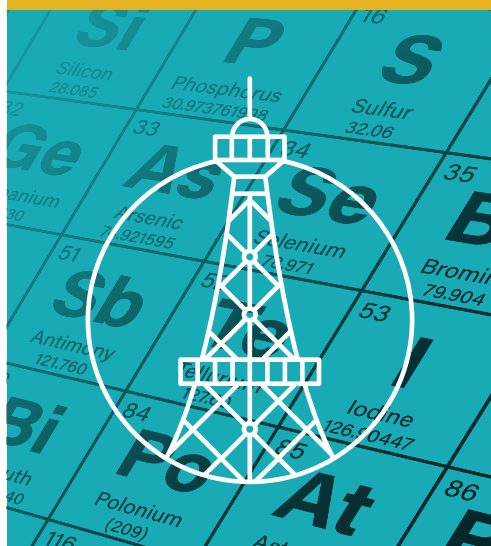
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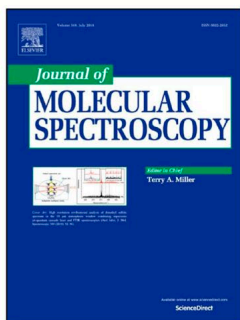


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The *Journal of Molecular Spectroscopy* presents experimental and theoretical articles on all subjects relevant to molecular spectroscopy and its modern applications. An international medium for the publication of some of the most significant research in the field, the *Journal of Molecular Spectroscopy* is an invaluable resource for astrophysicists, chemists, physicists, engineers, and others involved in molecular spectroscopy research and practice.

Feature Articles:

It is planned to have several peer reviewed Feature articles in the *Journal of Molecular Spectroscopy* each year. These articles will overview areas of particular significance in molecular spectroscopy. They may review and consolidate an area of theoretical development or a collection of experimental data, in each case offering some new insights. The articles may also summarize the present status of a rapidly developing and/or evolving field. All the articles should serve as introductions to areas of spectroscopy other than one's specialty and should be particularly valuable to students entering the field.

Feature articles will be solicited by invitation of the Editor. However, the Editor invites suggestions, with a reasonable level of detail, about topics that could be of interest. Self-suggestions by potential authors are particularly encouraged.



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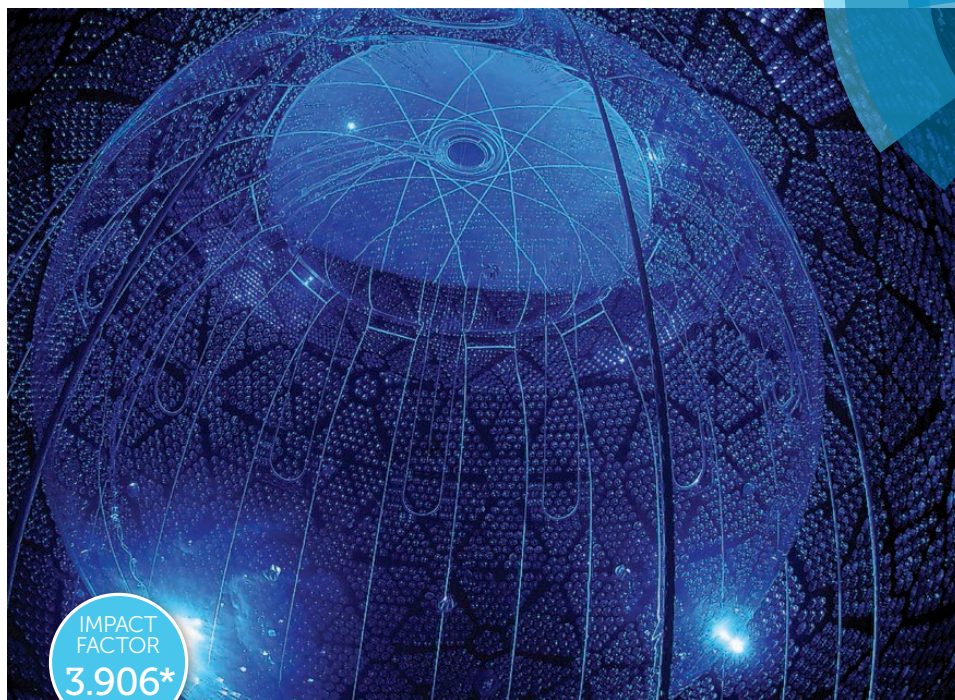


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A structural and molecular physical database with data excerpted from microwave spectroscopy, molecular radio astronomy and gas-phase electron diffraction

Example of a Compound Entry:

Document 4 of 4
CN 127415 (30281) MOGCOM2017 - Copyright © 2018 University of Ulm
MF C5 H6 N2 O2
RN 65.71.4
NA 5-Methyl-2,4(1H,3H)-pyrimidinedione
5 Methyl-1H-pyrimidin-2,4-dione
Thymine
LC 114057
UP 14.02.2017

Last changes at 17.10.2009

Last changes at 17.10.2010

[Show three dimensional molecular structure](#) (Last changes at 28.10.2010)

Method of study: Microwave Spectroscopy
ab initio Calculations

Refined geometrical parameters:
Errors of values are parenthesized in units of the last digit.

Structure type for distances: (r-e-se)

Parameter(s)	Value(s) (Angstroem)	Note(s)
N1-C2	1.3782 (10)	*
C2-N3	1.3797 (9)	

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NOTE: The parameters measured in this 3D viewer could only be approximate!

C(6)-C(5)-C(9)-H(15): Dihedral Angle = 120.8°

New Features of the 3D Applet

It is now possible to define:

- centroids and least-squares planes for groups of atoms (e.g. rings) and "measure":
- distances between centroids and atoms
- distances between least-squares planes and atoms
- angles between least-squares planes
- distances between atoms/centroids and inertial axes
- angles between bonds and axes
- angles between least-squares planes and axes

Ref.: N. Vogt, J. Demaison, D. N. Ksenafontov and H. D. Rudolph: J. Mol. Struct. **1076** (2014) 483-489

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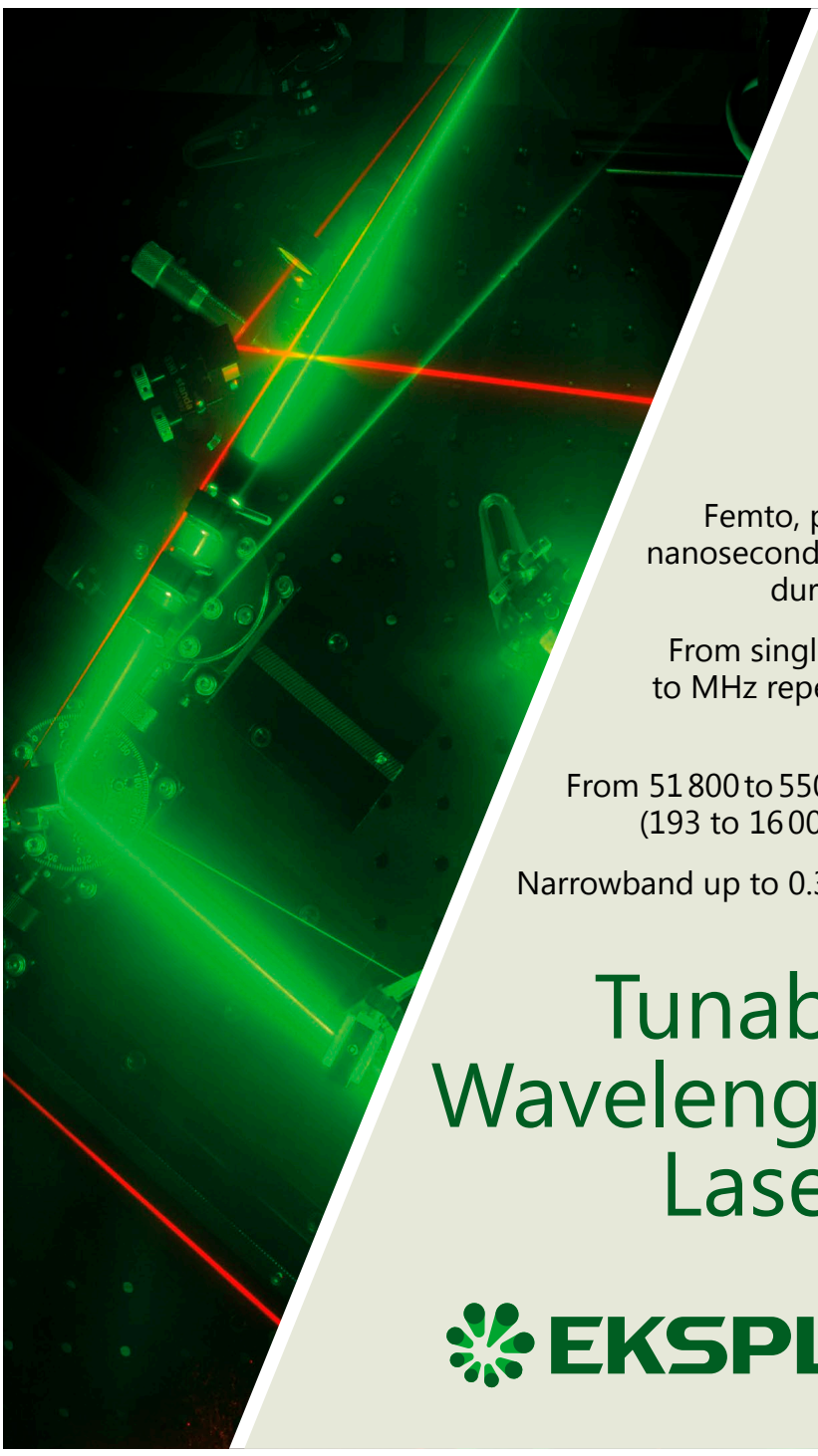
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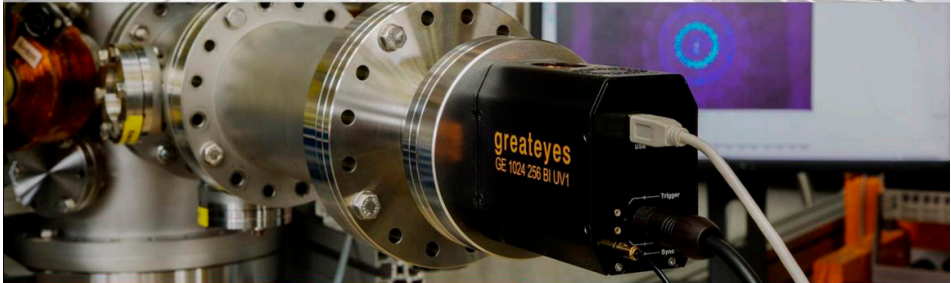
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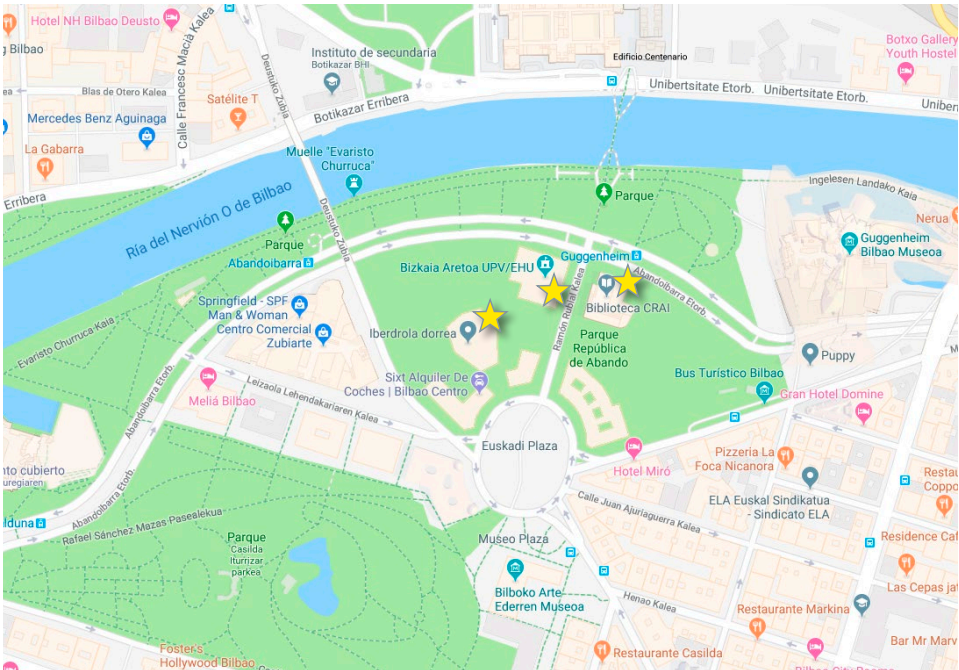
Conference Venue

Bilbao

Bilbao is the capital of Biscay and the largest metropolitan area in the Basque Country and the north of Spain. Founded in 1300, the city soon became a commercial port and sea hub, gaining significant importance from iron ore export. Bilbao went through a heavy industrialisation and steady economic development since the XIX century. Nowadays, Bilbao has turned into a vigorous city, strongly positioned in the service sector, experiencing an ongoing social, economic, and aesthetic revitalisation process. Bilbao received the inaugural Lee Kuan Yew World City Prize Laureate in 2010 in recognition of its integrated and holistic approach to urban transformation. Just recently, the town was named European City of the Year at the 2018 Urbanism Awards. Bilbao can conveniently be reached by air, sea or land (plane, ship, train or car).

Conference Venue

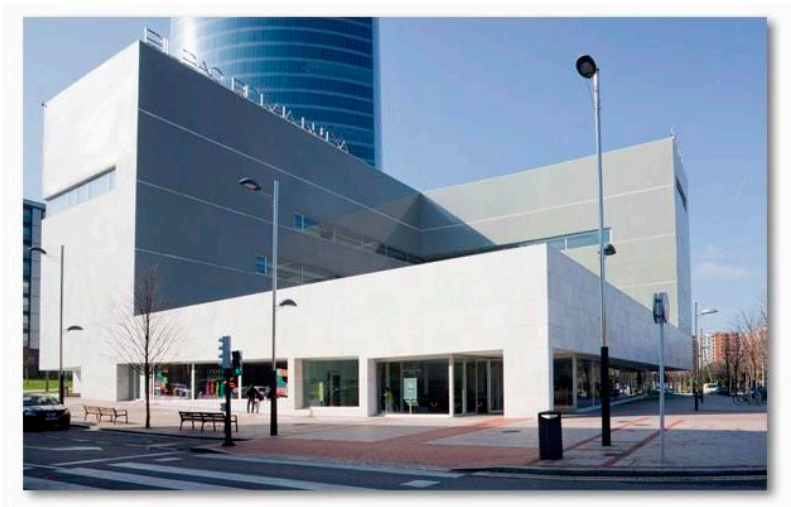
The Conference will be held at the “*Bizkaia Aretoa*” or Biscay Hall, a new building designed by the Pritzker prize winning architect Alvaro Siza. The Biscay Hall is located within the Bilbao city center, in the vicinity of the Guggenheim Museum and close to other major city sights. The building comprises the “*Mitxelena*” Auditorium, with capacity for 441 persons, several other lecture halls and exhibition rooms, which will be available for the meeting.



Map of Bilbao showing the Conference Venue (Bizkaia Aretoa) and the two affiliate restaurants.

The Conference building covers over 9,000 square meters, distributed over six floors. During the event, the rooms of the Bizkaia Aretoa are assigned as follows:

TECHNICAL SECRETARIAT	Main Hall		Ground Floor
PLENARY SESSIONS	Mitxelena Room	441 persons	Ground Floor
ORAL SESSIONS			
A Sessions	Mitxelena Room	441 persons	Ground Floor
B Sessions	Baroja Room	161 persons	Second Floor
C Sessions	Oteiza Room	96 persons	First Floor
POSTER SESSIONS			
Tuesday and Thursday sessions	Axular Room	also afternoon coffee break on Tuesday	First Floor
Tuesday and Thursday sessions	Chillida Room	also afternoon coffee break on Thursday	First Floor
Exhibition & Services			
Company stands and morning coffee breaks	Main Hall	also afternoon coffee break on Wednesday	Ground Floor
Working space	Elhuyar Room		First Floor
Meeting space	Laboa Room		Second Floor



Conference building: Bizkaia Aretoa – UPV/EHU (Abandoibarra Avenue 3, 48009 Bilbao)

Affiliate restaurants

Lunch tickets are available from the conference's registration web-site. Dinners are not organized by the conference.

The Conference will have **two affiliate restaurants**, located in the **Iberdrola Tower** and the **Deusto Library (CRAI)**, two of the more modern buildings of the city and both within five-minute walking distance from the venue (pictures below). You will have the option to try some traditional menus while enjoying the views of the Abandoidarra avenue. The lunch tickets will be color-coded (black/white), assigning them to one of the two restaurants. For dinners, you are referred to the great variety of dining opportunities all around in downtown Bilbao.



Iberdrola Tower and lunch ticket



Deusto Library (CRAI) and lunch ticket

Social program

A **Social Program for accompanying persons** is offered on the conference's web-site, including two excursions.

The registration for the tours continues to stay open, but we ask you to sign-up before **August 10th** to make sure that a minimum of 10 persons is reached for each tour. Tours with lower demand will have to be cancelled. Sometime in August we will inform you on the booking status of the tours.

Late registration

Late registration will be possible until the opening of the Conference. Please visit the conference's web-site for more information.

How to get to Bilbao

BY AIR

The **airport of Bilbao** is located at 12km away from Bilbao.

BY BUS

There is a **bus service** (Bizkaibus) that links the city with the airport every 20 minutes and with several stops in the Bilbao city center (Line A3247: Bilbao–Aeropuerto). Bus tickets are directly available from the driver. The bus ticket is around 3 euros (big notes are not allowed).

At the airport, the bus departures are in front of the Arrivals Terminal. The stops in Bilbao include: 1) Alameda Recalde, 14; 2) Gran Vía (Regional Government Office), and 3) Gran Vía, 74.

The final stop is the Bus Terminal ("Termibus", Garellano street, 1), and provides additional connections with the underground trains (Metro Bilbao, San Mamés station), regional trains (Euskotren) and Spanish trains (Renfe).

The bus service between the city and the airport starts at the Bus terminal and has intermediate stops in: 1) Gran Vía, 79; 2) Plaza Moyua, and 3) Alameda Recalde, before reaching the airport.

BY TAXI

The trip from the airport to Bilbao takes over 15–20 minutes. Taxis are located in front of the Arrivals Hall. A ride to the center of Bilbao costs around 25€.

BY LAND

The **AP–8 motorway** (part of **E–5**, **E70** and **E–80**) goes to Donostia/San Sebastian and Irun, and continues on to Bordeaux and Paris.

The **AP–68 motorway (E–804)** links with central Spain, Madrid and Portugal

BY TRAIN

Medium- and long-distance trains, operated by RENFE, arrive at main railway station ("Abando Indalecio Prieto Station"), in the city center. Other short-distance and regional trains operated by **Euskotren** and **Ferve** connect to regional destinations in Northern Spain.

More information: <http://www.renfe.com/EN/viajeros/index.html>

BY BUS

National and international buses with destination to Bilbao arrive at the Bilbobus bus terminal (Garellano Street, 1).

More information:

<http://www.termibus.es/lang/en/index.php> <https://www.alsa.es/en/home>

BY SEA

Ferries from the UK (Porstmouth) arrive at the Santurtzi terminal (14 km from Bilbao) three times a week, carrying people and vehicles.

More information: <http://www.brittany-ferries.co.uk/>

Moving around

METRO

There are three different lines of metro (subway). During the week the metro operates from 6:00 to 23:00 h. On weekends the metro offers a special night-time service. On Fridays the Metro works until 2:00 in the morning and on Saturdays it has a 24h service.



BY TRAM

The Bilbao tram (EuskoTran) was born to improve the railway services in Bilbao and to serve neighbourhoods and areas unattended by Metro Bilbao or short-distance trains. The construction of the first phase of the line started on May 1999. The first six stations were opened on December 18, 2002. Bilbao Tram line Atxuri-La Casilla, works from 6:00 to 23:00 during the week and from 07:00 to 23:30 on weekends. The nearest station to the conference venue is: Guggenheim.

BY BUS

The metropolitan bus service in Bilbao is called Bilbobus, and comprises 148 bus lines and 517 stops all around the city. Bilbobus offers a variety of lines to move around the city.

→ www.bilbao.eus/bilbobus

BY TAXI

Radio Taxi Bilbao: +34 94 444 88 88

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Tips for Bilbao

- While there is no official language, the typical **language of the Conference will be English**. The Basque Country has two official languages: Spanish and Basque.
- In many streets you will be able to **access Internet** through the City Hall public system [Bilbao Wifi].
- The phone number for all kinds of **emergencies**, such as urgent medical care, ambulances, police and firefighters is 112.
- Before departing from abroad, check that your insurance policy covers your travel to and within Europe.
- **Electrical plugs** in Spain are of European type F (220 Volt, 50Hz). You should review if and what type of adaptor you need for the electrical equipment brought with you. Modern computers and some other appliances accept both 220 V and 110 V automatically, but double-check the electrical requirements for any device individually.
- The Euro is in circulation as Spain's **currency**.
- **Meals:** The typical times in Spain for meals are:
 - Breakfast: from 8:00 to 10:00 h.
 - Lunch: from 13:30 to 15:00 h.
 - Dinner: from 20:30 to 22:30 h.
- **Smoking** is not permitted in the bars or cafes.
- **Banks:** Monday to Friday from 08:30 to 14:00 h.
- **Shops:** Open Monday to Saturday from 10:00 to 13:30/14:00 h. and from 16:30 to 20:00 h. Shopping centers, large department stores, but only some of the other stores do not close at midday and are open until 22:00 h. Generally, stores do not open on Sundays.

Tourist information

Bilbao has a huge patrimony distributed along the three main areas of the city:

THE CASCO VIEJO (Old Quarter, or The Seven Streets)

It is the oldest neighbourhood and the original nucleus of Bilbao. Apart from the Seven Streets, the most ancient streets of the city, the Old Town holds the Plaza Nueva, the Arriaga Theatre, Bidebarrieta Library, the Bilbao Stock Exchange, Atxuri railway station, Santiago Cathedral and the churches of San Antón, San Nicolás and Santos Juanes. Its commercial strength is reflected in five hundred shops, most importantly the Ribera Market, the largest indoor food market in Europe.

GRAN VÍA DON DIEGO LÓPEZ DE HARO (Great Avenue Diego López de Haro)

It is the commercial and financial area of Bilbao, with the buildings of the banks BBVA, BBK and Caja Laboral, the El Corte Inglés department store, the Headquarters of the Regional Government of Bizkaia and the Sota Building. Before the halfway point is the Plaza de Federico Moyúa, the heart of the Ensanche district of Bilbao, home to the Chavarri Palace and the Hotel Carlton.

ABANDOIBARRA and RÍA DE BILBAO (Abandoibarra and Bilbao estuary)

On the right side of the river you can find the Town Hall of Bilbao and at the end of the Volantín field, The Olabarri Palace. On the other side and crossing the Zubi Zuri or White Bridge, the Isozaki towers (Isozaki Atea) and the Guggenheim Museum Bilbao can be found. The Padre Arrupe walkway leads to University of Deusto and Deusto Bridge. Continuing along the promenade will reach the Euskalduna Congress Palace and the Maritime Museum.

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Bilbao 2018 September 3rd-7th
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