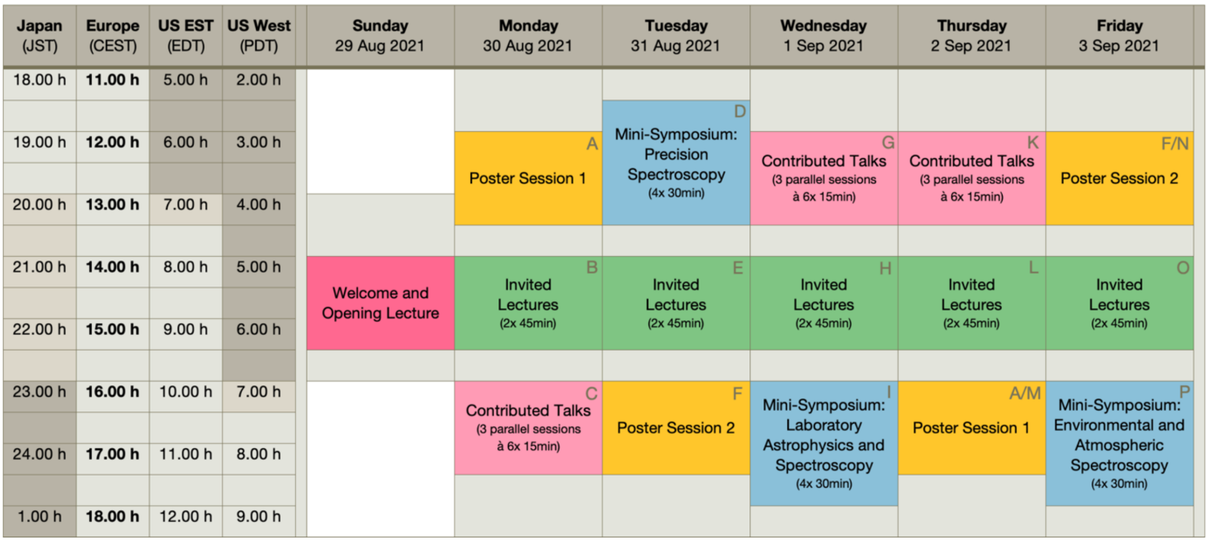
Book of Abstracts 27th Colloquium on High-Resolution Molecular Spectroscopy (HRMS Cologne 2021)

The 27th Colloquium on High-Resolution Molecular Spectroscopy (HRMS) was initially planned on-site. Due to the Covid-19 pandemic, the event is held for the first time as an online conference to fulfill the regulations of the government and to facilitate safe exchange of scientific information.

There are 11 invited lectures and 3 mini-symposia. Parallel sessions feature 54 contributed lectures given by PhD students and postdocs. 4 poster sessions are planned. The scientific fields covered are:

- High resolution rotational, vibrational, and electronic spectroscopy of molecules (radicals, ions, complexes, clusters, ...)
- Molecular dynamics
- Theory assisting the prediction, simulation, and interpretation of spectra
- New techniques for high-resolution spectroscopy
- Applications to atmospheric sciences, astrophysics, planetology, combustion, gas-phase biomolecules, metrology and fundamental physics, cold molecules, etc.

Program Overview



Japan (JST)	Europe (CEST)	US EST (EDT)	US West (PDT)	Sunday 29 Aug 2021	Monday 30 Aug 2021	Tuesday 31 Aug 2021	Wednesday 1 Sep 2021	Thursday 2 Sep 2021	Friday 3 Sep 2021
18.00 h	**11.00 h**	5.00 h	2.00 h						
						D Mini-Symposium: Precision Spectroscopy (4x 30min)			
19.00 h	**12.00 h**	6.00 h	3.00 h		A Poster Session 1		G Contributed Talks (3 parallel sessions à 6x 15min)	K Contributed Talks (3 parallel sessions à 6x 15min)	F/N Poster Session 2
20.00 h	**13.00 h**	7.00 h	4.00 h						
21.00 h	**14.00 h**	8.00 h	5.00 h	Welcome and Opening Lecture	B Invited Lectures (2x 45min)	E Invited Lectures (2x 45min)	H Invited Lectures (2x 45min)	L Invited Lectures (2x 45min)	O Invited Lectures (2x 45min)
22.00 h	**15.00 h**	9.00 h	6.00 h						
23.00 h	**16.00 h**	10.00 h	7.00 h		C Contributed Talks (3 parallel sessions à 6x 15min)	F Poster Session 2	I Mini-Symposium: Laboratory Astrophysics and Spectroscopy (4x 30min)	A/M Poster Session 1	P Mini-Symposium: Environmental and Atmospheric Spectroscopy (4x 30min)
24.00 h	**17.00 h**	11.00 h	8.00 h						
1.00 h	**18.00 h**	12.00 h	9.00 h						

Program, Sunday, August 29, 2021

14.00	**Welcome Address by the organizers** ***Prof. Stephan Schlemmer***, I. Institute of Physics, University of Cologne, Germany Chair of HRMS 2021 ***Prof. Frédéric Merkt***, Laboratory Physical Chemistry, ETH Zürich, Switzerland Member of the HRMS Executive Committee
14.10	**HRMS 2021 Opening Lecture** ***Pascale Ehrenfreund***, Space Policy Institute, George Washington University, U.S.A. «The search for life in our Solar System»
15.00	**International Dr. Barbara Mez-Starck Prize 2021** ***Dr. Jürgen Vogt,*** Member of the presiding board of the Dr. Barbara Mez-Starck-Foundation, Announcement of two laureates of the international Dr. Barbara Mez-Starck Prize for structural chemistry and molecular physics
15:20	End of day 1

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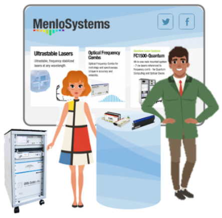


The search for life in our Solar System

P. Ehrenfreund[1,2]

[1]Space Policy Institute, George Washington University, [2]Leiden Observatory

One of the most fascinating questions in planetary science is how life originated on Earth approximately 3.5-3.7 billion years ago and whether life exists beyond Earth. Life on Earth has adapted to nearly every explored environment including the deep ocean, dry deserts and ice continents. What were the chemical raw materials available for life to develop? What role did small Solar System bodies play in the delivery of raw material for life during the heavy bombardment phase in the early history of our Solar System. Where can we find life or remnants of life in our Solar System considering the progress and data on “extreme life” on Earth that has transformed our view of habitability.

A fleet of present and future robotic space missions target planets and moons in order to assess their habitability and to seek biosignatures of simple extraterrestrial life beyond Earth. Prime future targets in the outer Solar System include moons that may harbor internal oceans such as Europa, Enceladus, and Titan. Life may have emerged during habitable periods on Mars and evidence of life may still be preserved in the subsurface, caves, or evaporite deposits. Several orbiters as well as the Insight lander and the Curiosity rover are exploring Mars. In 2021, three additional robotic missions arrived at Mars. China’s ambitious Tianwen-1 mission composed of an orbiter, lander and rover landed its rover Zhurong in May 2021 in Utopia Planitia. The United Arab Emirates orbiter “Hope” is starting its scientific measurements of the Martian atmosphere. NASA’s Mars2020 mission Perseverance rover landed in the Jezero crater and will collect material for a future Mars sample return mission. Mars is still the central object of interest for habitability studies and life detection beyond Earth, paving the way for returned samples and human exploration.

Extensive science activities in support of planetary exploration are performed worldwide in the laboratory, in the field and through simulation studies. Life detection strategies need to be robust to recover traces of biomarkers and are critically dependent upon the sensitivity of detection methods. This lecture will discuss the current results of Mars missions and discuss the science and technology preparation crucial for robotic and human exploration efforts investigating habitability and biosignatures in our Solar System.

Program, Monday, August 30, 2021

12.00	**Poster Session 1** Watch the short video presentations Meet the poster presenters on the interactive platform MeetAnyway
13.30	Break
	Invited Lectures (B) Chair: Attila Császár, Eötvös University, Hungary
14.00	***Ad van der Avoird***, Radboud Universiy, Nijmegen (NL) «Para-ortho hydrogen conversion; solving a 90-year old mystery» Molecular Physics Lecture
14.45	***Edit Mátyus***, ELTE «Recent developments and future challenges in molecular quantum theory»
15.30	Break

Contributed Talks (C)

	Internal Rotation (CA) Chair: Vadim Ilyushin, The National Academy of Sciences of Ukraine	**Infrared (CB)** Chair: Oskar Asvany, Universität zu Köln, Germany	**Theory (CC)** Chair: Sergey Yurchenko, University College London, UK
16.00	***Thomas C. Salomon***, Universität zu Köln «Internal rotation in a loosely bound ion-rare-gas complex: He-H_3^+»	***Sathapana Chawananon***, Sorbonne Université «High resolution rovibrational spectroscopy of bicyclic aromatic hydrocarbons»	***Kamil Stankiewicz***, Nicolaus Copernicus University «Investigation of collisional effects in molecular spectra - accurate ab initio calculations in HD-He system»
16.15	***Safa Khemissi***, Université Paris-Est Créteil «Methyl internal rotations and ^{14}N quadrupole coupling in the microwave spectra of 2,4-dimethylthiazole and 4-methyl-5-vinylthiazole»	***Shreyak Banhatti***, Universität zu Köln «Acetylene loss from anthracene and phenanthrene cations»	***Victoria H.J. Clark***, Univerity College London «Calculating the non-LTE spectra of small molecules using the ExoMol Database»
16.30	***Pascal Stahl***, University of Kassel «Spectroscopy on the first excited torsional state of propylene oxide»	***Irén Simkó***, ELTE Eötvös Loránd University «Structure and dynamics of the semirigid HHe_2^+ and the fluxional HHe_3^+ cations»	***Kevin Gregor Lengsfeld***, Gottfried-Wilhelm-Leibniz-Universität Hannover «A Quantum Chemical Method Producing Accurately Predicted Barrier Heights to Methyl Group Internal Rotation - The Test Case of Acetylspecies»
16.45	***Iwona Gulaczyk***, Adam Mickiewicz University «IR Rotational Spectrum of Methylamine»	***Aleksandr Andreevich Balashov***, Nicolaus Copernicus University «Oxygen B-band P-branch study: simultaneous observation of Dicke narrowing and speed-dependence effects»	***Carlos Murilo Romero Rocha***, Leiden University «High-Level Ab Initio Quartic Force Fields and Spectroscopic Characterization of C_2N^-»
17.00	***Christina Dindic***, RWTH Aachen University «The effects of two inequivalent internal rotations in acetylmethylthiophenes explored by microwave spectroscopy»	***Alexander Petrovich Kouzov***, Saint-Petersburg State University «Satellites in Infrared and Raman Spectra of Linear Molecules»	***Miguel Sanz-Novo***, Universidad de Valladolid «Unveiling the Shape of Neutral Levodopa»
17.15	***Luyao Zou***, Universite de Lille «Analysis of the low torsional barrier of a heavy C3v top: the case of trifluroacetic acid»	***Marcos Juanes***, University of Valladolid «Observation of Selenium-centered Hydrogen Bonds by Jet-Cooled Microwave Spectroscopy: Benzeneselenol ··· H_2O vs.	***Andrei Vladimirovich Sokolov***, Saint-Petersburg State University «Energy-Corrected Sudden approach to the non-Markovian relaxation matrix for two linear colliders»
17.30	End of day 2		

Beyond the horizon: HITRAN2020 and HITEMP data for planetary atmospheres

R. J. Hargreaves[1], R. Hashemi[1], E. V. Karlovets[1], E. K. Conway[1], F. Skinner[1], A. A. Finenko[2,1], K. Nelson[1], Y. Tan[3,1], R. V. Kochanov[4,1], I. E. Gordon[1]*, L. S. Rothman[1]*

[1]Harvard-Smithsonian Center for Astrophysics, [2]Moscow State University, Moscow, Russia, [3]USTC, Hefei, China, [4]V.E. Zuev Institute of Atmospheric Optics, Tomsk

The recently-released 2020 edition of the HITRAN database has continued efforts to include and improve appropriate spectroscopic data for studying a variety of planetary atmospheres. In particular, line lists for key atmospheric species (e.g., SO_2, NH_3, C_2H_2, PH_3) have received substantial updates, compared to HITRAN2016 [1], which include extending spectral coverage and improving line positions, intensities, and broadening coefficients. There are currently 55 molecules with line-by-line parameters in HITRAN, with new species being included for HITRAN2020 that have particular relevance to planetary atmospheres (e.g., GeH_4, CS_2, SO). Furthermore, additional planetary-relevant absorption cross-sections and collision-induced absorption data are now included. Pressure-broadening parameters (and their temperature dependencies) for H_2, He, CO_2 and H_2O are also provided for numerous species, allowing opacities to be calculated using HITRAN data for a variety of planetary atmospheres, including Venus, Mars, and Jupiter.

The temperature range of planetary atmospheres can substantially exceed those found on Earth, therefore it is necessary to account for significantly more transitions when modelling high-temperatures environments. In addition, high-resolution observations require accurate spectroscopic parameters to enable characterization of these atmospheres. The HITEMP database [2] provides line-by-line parameters for use at high temperature and has recently been undergoing a significant upgrade. HITEMP line lists are now available for N_2O, NO_2 [3] and CH_4 [4], while the CO, NO and OH line lists have been updated [3,5]. For CH_4, an intensity compression technique has been introduced that is capable of being accurate at modelling high-temperature spectra, and also practical to use [4].

The additions of planetary-relevant molecules and spectroscopic parameters for HITRAN2020 will be discussed, along with recent updates to the HITEMP database. Note that a companion poster by I. Gordon will discuss the improvements in HITRAN2020 that are relevant to the remote sensing of terrestrial atmosphere.

[1] I. E. Gordon, et al., *J. Quant. Spectrosc. Radiat. Transfer*, **2016**, 203, 3-67.

[2] L. S. Rothman, et al., *J. Quant. Spectrosc. Radiat. Transfer*, **2010**, 111, 2139-2150.

[3] R. J. Hargreaves, et al., *J. Quant. Spectrosc. Radiat. Transfer*, **2019**, 232, 35-53.

[4] R. J. Hargreaves, et al., *Astrophys. J. Supp. Ser.*, **2020**, 247, A55.

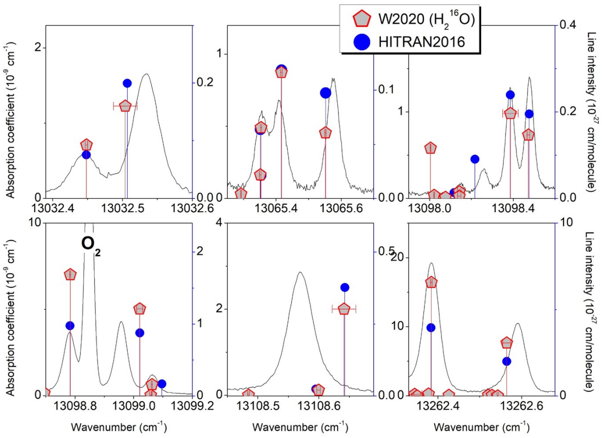
[5] G. Li, et al., *Astrophys. J. Supp. Ser.*, **2015**, 216, A15.

Water vapor absorption in the region of the oxygen A-band near 760 nm

S. Vasilchenko[1], S. Mikhailenko[1,3], A. Campargue[2]

[1]V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of Science, 1, Academician Zuev square, 634055 Tomsk, Russia, [2]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France , [3] Climate and Environmental Physics Laboratory, Ural Federal University, 19, Mira av., 620002 Yekaterinburg, Russia

The oxygen A-band near 760 nm is used to determine the air-mass along the line of sight from ground or space borne atmospheric spectra. This band is located in a spectral region of very weak absorption of water vapor and interfering lines of atmospheric water vapor are expected to have a small impact on the retrieved air-masses. The increased requirements on the determination of the air columns make nevertheless suitable to accurately characterize water absorption spectrum in the region. In the present work, we use cavity ring down spectroscopy (CRDS) to measure with unprecedented sensitivity and accuracy the water spectrum in the 12,970 - 13,170 cm^{-1} region. A total of about 730 water lines were determined and rovibrationally assigned leading to the determination of 76 new levels and correction of 61 levels of $H_2{}^{16}O$. Spectroscopic line lists available in the region - HITRAN, W2020 and theoretical line lists - show important deviations compared to observations (see Fig). In particular, line intensities are poorly predicted by available *ab initio* calculations in the considered region involving transitions corresponding to a highly bending excitation.



Temperature-dependence of CH_3I line broadening by main atmospheric perturbers

J. Buldyreva[1], A. Dudaryonok[2], N. Lavrentieva[2], L. Troitsyna[1], N. Filippov[3]

[1]Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 Route de Gray, 25030 Besançon, France, [2]Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS,1 Akademician Zuev Sq., 634055 Tomsk, Russia, [3]Laboratory of Molecular Spectroscopy, Faculty of Physics, Saint-Petersburg State University, 3 Ulyanovskaya str, 198504 Saint-Petersburg, Russia

Reliable modelling of radiative transfer in the terrestrial atmosphere requires precise knowledge of spectroscopic parameters even for minor compounds such as methyl iodide. Besides its role in the ozone layer depletion [1,2], this gas is especially perilous for human health, so that atmospheric monitoring is also needed for CH_3I accidentally released into the atmosphere. The most convenient for atmospheric detection is the rather strong ν_6 fundamental at 892.916 cm^{-1}, which falls in the 11μm transparency window [3]. To the best of our knowledge, the line-shape parameters of methyl iodide have been studied experimentally solely at room temperature, whereas a larger temperature interval is required.

For the self-broadening case, we recently published theoretical estimates of line-broadening coefficients and their temperature-dependence parameters in the ν_6 band for the temperature range 200-400K [4]. The present work completes this previous investigation by considering the main atmospheric perturbers. The semi-empirical method [5] is employed, since for many molecular systems its model parameters were shown to be temperature independent. In this way, the 5 parameters c_1-c_5 obtained from fits on some room-temperature measurements are used to calculate line-broadening coefficients for 5 temperatures in the range 200-400K; the temperature-dependence characteristics are further deduced using the traditional exponential law and/or the recently suggested double-power law [6].

[1] D. Davis, J. Crawford, S. Liu, S. McKeen, A. Bandy et al., *Journal of Geophysical Research: Atmospheres*, **1996**, 101(D1), 2135-47. [2] S. Solomon, R. Garcia, A.R. Ravishankara, *Journal of Geophysical Research: Atmospheres*, **1994**, 99(D10), 20491-20499. [3] P. Bernarth, *Optics & Photonics News*, **2015**, 16, 18–23. [4] L. Troitsyna, A. Dudaryonok, J. Buldyreva, N. Filippov, N. Lavrentieva, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **2020**, 242, 106797. [5] A.D. Bykov, N.N. Lavrentieva, L.N. Sinitsa, *Molecular Physics*, ***2004**,* 102, 1653–1658. [6] R.R. Gamache, B. Vispoel, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **2018**, 217, 440-452.

Nitrogen-broadening coefficients for the CH_3I ν_6 fundamental

J. Buldyreva[1], L. Troitsyna[1], A. Dudaryonok[2], N. Lavrentieva[2], N. Filippov[3]

[1]Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 Route de Gray, 25030 Besançon, France, [2]Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS, 1 Akademician Zuev Sq., 634055 Tomsk, Russia, [3]Laboratory of Molecular Spectroscopy, Faculty of Physics, Saint-Petersburg State University, 3 Ulyanovskaya str, 198504 Saint-Petersburg, Russia

Necessity of improving methyl iodine line-shape parameters and creating line-lists for databases [1-4] arise from crucial needs of monitoring CH_3I accidentally released into the atmosphere. A particular interest for atmospheric detection of CH_3I represents its rather strong ν_6 fundamental located at 892.916 cm^{-1} and falling in the 11μm transparency window [5]. Besides the self-broadening case analysed previously at room temperature [4] and in the temperature range 200-400K [6], the case of perturbation by nitrogen is worthy of consideration.

The present work focuses on theoretical estimates of CH_3I-N_2 line-widths at the room temperature of 296K. As in [4,6], a semi-classical (SC) and a semi-empirical (SE) methods are employed to get the line-broadening coefficients for the 6 sub-branches of the ν_6 band with the rotational quantum numbers $0 \leq J \leq 70$ and $K \leq 20$ requested typically for spectroscopic databases. The SC method uses exact classical trajectories governed by the isotropic potential [7] and accounts for long-range and short-range interactions. The SE approach corrects the analytical expressions of the Anderson-theory by an empirically adjusted factor [8], with the intermolecular potential represented by long-range forces only. Theoretical results are compared to available measurements for the ν_6 [9] and ν_5 fundamentals [10], showing a very satisfactory agreement and a clearly negligible vibrational dependence.

[1] A. Perrin, I. Haykal, F. KwabiaTchana, L. Manceron, D. Doizi, G. Ducros, *Journal of Molecular Spectroscopy*, **2016**, 324, 28–35. [2] I. Haykal, D. Doizi, V. Boudon, A. El Hilali, L. Manceron, G. Ducros, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **2016**, 173, 13–19.
[3] F. KwabiaTchana, Y. Attafi, L. Manceron, D. Doizi, J. Vander Auwera, A. Perrin, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **2019**, 222–223, 130–137. [4] E. Raddaoui, L. Troitsyna, A. Dudaryonok, P. Soulard, M. Guinet, H. Aroui, J. Buldyreva, N. Lavrentieva, D. Jacquemart, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2019, 232, 165–179. [5] P. Bernarth, *Optics & Photonics News*, **2015**, 16, 18-23. [6] L. Troitsyna, A. Dudaryonok, J. Buldyreva, N. Filippov, N. Lavrentieva, *Journal of Quantitative Spectroscopy and Radiative Transfer*, **2020**, 242, 106797. [7] J. Buldyreva, L. Nguyen, *Physical Review A*, **2008**, 77, 042720. [8] A.D. Bykov, N.N. Lavrentieva, L.N. Sinitsa, *Molecular Physics*, **2004**, 102, 1653-1658. [9] Y. Attafi, A.B. Hassen, H. Aroui, F. KwabiaTchana, et al. *Journal of Quantitative Spectroscopy and Radiative Transfer*, **2019**, 231, 1-8. [10] K. Hoffman, P. Davies, *Journal of Molecular Spectroscopy*, **2008**, 252, 101-7.

The conformational behaviour of dicarboxylic acid monomers and complexes revealed by rotational spectroscopy

C. Medcraft[1], M. Schnell[2,3]

[1]UNSW Sydney, [2] Deutsches Elektronen-Synchrotron DESY, Hamburg, G, [3]Institut für Physikalische Chemie, Christian-Albre

Secondary organic aerosols (SOA) play a crucial yet uncertain role in Earth's climate that are formed from the gas phase oxidation products of organic compounds. Di-carboxylic acids are ubiquitous in SOA[1] and have been shown to have significant conformer dependant atmospheric reactivities.[2] The dimerization and complexation with other atmospheric molecules is dependent on the balance between inter- and intra- molecular hydrogen bonding and is thus highly influenced by the conformation of the monomers. Despite their importance in the atmosphere, gas phase spectroscopic data on these molecules is limited due, in part, to the difficulty in bringing them into the gas phase as they often decarboxylate or form anhydrides when heated. For example, malonic acid (propanedioic acid) fragments upon heating to give carbon dioxide and acetic acid.

Using chirped pulse Fourier-transform microwave spectroscopy in the 2-8 GHz and 18-26 GHz frequency ranges we have successfully detected the elusive Tt conformer of pyruvic acid (figure 1) and two conformers of malonic acid. Computational and experimental results on the homo- and hetero- dimers and hydration complexes of pyruvic acid and oxalic acid will also be presented

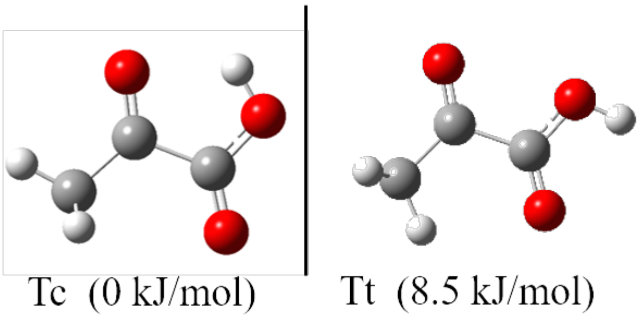


Figure 1: The two lowest energy conformations of pyruvic acid. Note that the higher energy Tt conformer has a H-bond available for intermolecular bonding, these conformers become essentially isoenergic (ΔE=1.7 kJ/mol) when a water molecule binds.

1. Meng, J. et al. Sci. Total Environ., 2020, 705, 135256. https://doi.org/10.1016/j.scitotenv.2019.135256.
2. Blair, S. et al. J. Phys. Chem. A, 2020, 124 (7), 1240–1252 https://doi.org/10.1021/acs.jpca.9b10613

The Soleil View on Dimethyl Ether

C. P. Endres[1], T. F. Giesen[2]

[1]Max Planck Institute for extraterrestrial Physics, Gießenbachstr. 1, 85748 Garching, Germany, [2] Universtiy of Kassel, Laboratory Astrophysics, Heinrich-Plett-Str. 40 34132 Kassel, Germany

Dimethyl ether (DME, CH3OCH3) is highly abundant in hot cores and numerous transitions not only within the vibrational ground state, but also within torsionally excited states, $v_{11} = 1$ @ 197.6 cm^{-1} and $v_{15} = 1$ @ 242.5 cm^{-1} , have been detected in interstellar line surveys, such as the high-mass star-forming region G327.3-0.6 [1]. New observations of G327.3-0.6 show that vibrational satellites can be very intense and even the detection of other excited vibrational states, such as the COC bending state $v_7 = 1$ @ 412.4 cm^{-1} , might be possible.

However, analysis of the COC bending mode is quite challenging, because of the presence of various interactions with torsionally excited states. Therefore, the high resolution vibrational spectrum of dimethyl ether has been recorded in the far-IR using synchrotron-based Fourier transform spectroscopy, in addition to previous microwave measurements [2,3], which provides complementary information and in particular additional constraints on vibrational energies. Line assignments were performed using the Automated Spectral Assignment Procedure (ASAP) allowing accurate rotational energy levels of the lowest vibrations to be determined.

The paper will focus on the COC bending fundamental and will present the current state of the analysis of this ongoing project.

[1] Suzanne E. Bisschop, Peter Schilke, Friedrich Wyrowski et al., *Astronom. Astrophys.*, **2013,** 552, A122
[2] Christian P. Endres, Brian J. Drouin, John C. Pearson et al., *Astronom. Astrophys.*, **2009**, 504, 635-640
[3] Christian P. Endres, Holger S.P. Müller, Frank Lewen et al. *65th ISMS*, **2010**, abstract id FC01

Tunneling IAM treatment applied to the analysis of the CH_2OH radical sub-millimeter wave spectrum

L. H. Coudert[1], O. Chitarra[1], J. Spaniol[1], M. Martin-Drumel[1], O. Pirali[1], B. Gans[1], J. Loison[2]

[1]Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, France, [2]Intsitut des Sciences Moléculaires, Université de Bordeaux, Talence, France

Early *ab initio* calculations[1] revealed that the hydroxymethyl radical (CH_2OH) is a non-rigid species exhibiting a complicated potential energy surface. It displays 4 C_1 minima, 2 C_s local maxima, approximately 300 cm^{-1} above the minima, and 2 C_s maxima, approximately 1500 cm^{-1} above the minima. The large amplitude motion of the radical can be pictured as an internal rotation of the CH_2 group with respect to the OH group. The axis of internal rotation is the CO bond and the two-fold symmetry hindering potential is characterized by a barrier height of 1500 cm^{-1}. Aided by new *ab initio* results, the torsional levels associated with this torsional motion were computed. The calculated levels display a tunneling splitting which was found to be on the order of 2 cm^{-1} for the ground vibrational state.

In this poster, a line position analysis of already available[2,3] and newly measured sub-millimeter wave transitions will be reported for the CH_2OH radical. As its large amplitude motion seems to be well described by the high barrier approximation, the tunneling IAM water dimer formalism[4] was used to derive a fitting approach aimed at accounting for its rotation-tunneling energy. The effects of the fine spin-rotation and hyperfine spin-spin couplings, due to the unpaired electron, were also included.

The results of the analysis will be discussed and compared to those obtained with other approaches. The fitted values of the parameters describing the rotational dependence of the tunneling splitting will be compared to those retrieved theoretically from the geometry of the molecule along the tunneling path.[4]

[1] Saebø, Radom, and Schaefer, *J. Chem. Phys.,* **1983,** 78, 845-853; Marenich and Boggs, *J. Chem. Phys.,* **2003,** 119, 3098-3105; and *Ibid., J. Chem. Phys.,* **2003,** 119, 10105-10114

[2] Bermudez, Bailleux, and Cernicharo, *A&A,* **2017,** 598, A9

[3] Chitarra, Martin-Drumel, Gans, Loison, Spezzano, Lattanzi, Müller, and Pirali, *A&A,* **2020,** 644, A123

[4] Hougen, *J. Mol. Spectrosc.,* **1985,** 114, 395-426; and Coudert and Hougen, *J. Mol. Spectrosc.,* **1988,** 130, 86-119

Broadening of diffuse bands' profiles

J. Krełowski[1], G. A. Galazutdinov[2,4], P. Gnaciński[3], R. Hakalla[1], W. Szajna[1], R. Siebenmorgen[5]*

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland, [2]Instituto de Astronomia, Universidad Catolica del Norte, Antofagasta, Chile, [3]Institute of Theoretical Physics and Astrophysics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk, Poland, [4] Pulkovo Observatory, Saint-Petersburg , Russia, [5]European Southern Observatory, Garching, Germany

The paper describes profile broadening and positional displacements of diffuse interstellar bands (DIBs), seemingly caused by some physical properties of intervening clouds. Full width at the half maximum (FWHM) of four studied diffuse bands (5780, 5797, 6196 and 6614 Å) demonstrate strong variability, sometimes doubling the features' width. Despite of high magnitude of the effect [1], our current analysis is restricted to the strongest diffuse bands because the weaker ones require a much higher S/N ratio. The profile broadening in the studied DIBs evidently propagates towards longer wavelengths, probably due to the excitation of higher and higher levels of the P branch of the unknown molecular carrier. Moreover, diffuse bands are broader in clouds with abundantly populated vibrationally excited states of the hydrogen molecules, i.e. DIB's broadening correlates with the rotational temperaturę, estimated on H_2 $\nu=2$ vibrational level. However, the objects demonstrating extremely broadened profiles of DIBs are very scarce. The extreme peculiarity of DIBs' profiles was detected in the object Herschel 36. Here we show the gradual growths of the widths of diffuse bands, confirmed in spectra from different instruments. Our conclusions are based on the statistically significant sample of reddened stars.

Acknowledgements

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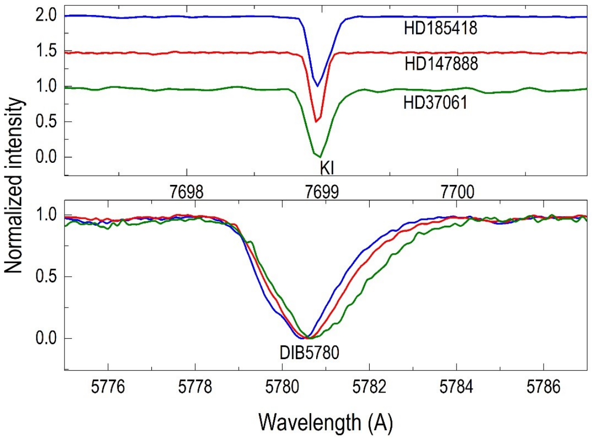

Fig.1 Physical (not related to Doppler splitting) broadening of the major 5780 DIB. Note the presence of positional displacement, apparently related to the profile width.

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On the Zeeman/Paschen-Back effect in the A-X system of CrH

A. J. Ross[1], J. Morville[1], P. Crozet[1], J. Morin[2]

[1]ILM, Université de Lyon, France, [2]LUPM, Université de Montpellier, France

Our work targets laboratory investigation of the magnetic response of CrH, whose (perturbed) A $^6\Sigma^+$ -X $^6\Sigma^+$ bands at 750 and 870 nm have been observed in the atmospheres of dwarf stars. Molecular signatures are becoming important in spectropolarimetric studies attempting to detect exoplanets around cool stars. Field-free line positions are well-documented [1-3] for the A-X system, with additional information for the ground state from microwave spectroscopy [4] and laser magnetic resonance studies [5]. The Zeeman effect has been investigated in molecular beam conditions (N =0, 1 only, in the A-X system) [6].

To extend these observations, we have recorded intracavity absorption and laser-induced fluorescence spectra at close to room temperature, partially resolving many Zeeman structures at magnetic fields up to 0.45 Tesla. Absorption spectra establish relative intensities; fluorescence spectra recorded with circularly polarised light reveal strong dissymmetry between σ^+ and σ^- transitions, as predicted [7] at modest magnetic field strengths with strong interactions between spin components. This dissymmetry is of specific interest for telescope spectropolarimetry, where Stokes V signals give a sensitive probe of stellar magnetism. CrH (and FeH) feature prominently in spectra of cool dwarf stars and brown dwarfs taken for example on the SPIRou instrument at the Canada-France-Hawaii telescope; accurate modelling of transitions is necessary for molecular data to be used to improve determinations of stellar radial velocities and discriminate stellar magnetism from exoplanet presence. We present results to date.

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Cold ion chemistry within a Rydberg-electron orbit: Test of the spectator role of the Rydberg electron in the He(n) + CO → C(n') + O + He reaction

F. B. V. Martins[1], V. Zhelyazkova[1], C. Seiler[1], F. Merkt[1]*

[1]ETH Zürich, Laboratory of Physical Chemistry

v class="ab-texts">
Ion-molecule reactions are usually challenging to study at low temperatures because ions are heated up by stray fields. To overcome this limitation, we study the ion-molecule reaction within the orbit of a highly excited Rydberg electron, making it possible to reach collision energies as low as ~k_{B}.100 mK [1-3]. We present experimental studies of the reaction between CO molecules and helium atoms excited to Rydberg-Stark states [He(n)] in a merged-beam apparatus. The supersonic beams of CO and of He(n) with principal quantum number n in the range 27–45 are merged using a surface-electrode deflector [4,5]. The reaction between a Rydberg atom and a molecule is expected to correspond closely to the ion-molecule reaction [6-8]. In the He(n) + CO reaction, long-lived atomic C(n') atoms are formed. This reaction system thus offers the possibility to study n-changing processes taking place before and during the reaction and to test the spectator role of the Rydberg electron.

We study the Rydberg-Stark-state distribution of the He(n) atoms and of the C(n') products experimentally by pulsed-field ionization and theoretically. The integrated signal from pulsed-field ionized He(n) and C(n') recorded with different electric field values is compared to the predicted diabatic ionization for a distribution of Rydberg-Stark states. The He sample initially excited to a specific n state is redistributed among a number of states prior to the reaction via fluorescence and blackbody-radiation-induced transitions during the 85-µs time between excitation and detection. We calculate the rates of these radiative processes and include them in Monte Carlo simulations to model the evolution of the He(n) population and its n-distribution. The agreement between the modeled ionization and the measured ionized He(n) signal confirms that a range of Rydberg-Stark states of He is populated. Discrepancies between experimental and modeled ionization of C(n') can be explained by the different ionization dynamics of C(n'). This finding indicates the validity of the Rydberg-electron-spectator model.

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New assignments and global analysis of the CD_2HOH rotation-torsion spectrum

L. H. Coudert[1], L. Margulès[2], R. A. Motiyenko[2], F. Kwabia-Tchana[3]

[1]ISMO, CNRS - Unisverité Paris-Saclay, 91405 Orsay France, [2]Université de Lille, Laboratoire de Physique des Lasers, [3]LISA, Université de Paris et Université Paris Est Créteil

Doubly deuterated methanol CD_2HOH is a non-rigid molecule displaying internal rotation of its asymmetrical CD_2H methyl group. Like the isotopic species of methanol with a symmetrical CH_3 or CD_3 group, it displays a strong rotation-torsion Coriolis coupling. Unlike these species, it also displays a dependence of its generalized inertia tensor on the angle of internal rotation. Its complicated rotation-torsion spectrum was investigated in the microwave,[1] sub-millimeter-wave,[2,3] terahertz,[2] and FIR[2,3] domains. Although more than 3000 transitions have been assigned so far, no global analysis, like the one performed for the analogous species CH_2DOH,[4] has been carried out.

In this poster, new assignments in the sub-millimeter, terahertz, and FIR spectra of CD_2HOH will be reported. The new parallel and perpendicular rotation-torsion transitions, assigned up $J = 35$, allow us to spectroscopically characterize torsional states with $0 \leq K \leq 12$ and $0 \leq v_t \leq 2$. Three line position analyses are carried out.

In the first one, restricted to rotation-torsion lines involving torsional states with $3 \leq K \leq 12$, rotational energies are evaluated with a $J(J+1)$ Taylor-type expansion for each torsional state. 4836 transitions were accounted for with a unit-less standard deviation of 12.8. In the second analysis, 124 torsional sub-band centers are fitted with an RMS of 0.048 cm^{-1} to obtain refined torsional parameters including the hindering potential. In the third analysis, 5907 rotation-torsion transitions involving torsional states with $0 \leq K \leq 12$, $0 \leq v_t \leq 2$, and $J \leq 26$ are reproduced with a unit-less standard deviation of 3.2 using the four-dimensional rotation-torsion fitting Hamiltonian developed for the mono-deuterated species.[4]

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Laboratory rotational spectroscopy of methyl n-propyl sulfide: Conformational analysis and methyl internal rotation

H. V. L. Nguyen[1], L. Tulimat[2], H. Mouhib[3], W. Stahl[2]

[1]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), [2]Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany, [3]Département Composants et Systèmes (COSYS), Laboratoire Instrumentation, Simulation et Informatique Scientifique (LISIS), Université Gustave Eiffel, 5 Boulevard Descartes, 77420 Champs-sur-Marne, Fran

The microwave spectrum of methyl n-propyl sulfide, CH_3-S-CH_2-CH_2-CH_3, was recorded in the frequency region from 2.0 to 26.5 GHz, revealing three conformers. Quantum chemical calculations were carried out to support the experimental work. Fine splittings arising from the internal rotation of the methyl group attached to the sulfur atom were resolved and analyzed. Torsional barriers of about 600 cm^{-1} for the two conformers with C_1 symmetry and about 700 cm^{-1} for the Cs conformer could be deduced, showing that the conformations affect the methyl internal rotation. Torsional splittings of the methyl group at the end of the propyl moiety were observed for some transitions, leading to the determination of barrier heights close to 1000 cm^{-1}. The spectrum of the 34S isotopologue of the most stable conformer could be measured in natural abundance. The present laboratory work provides highly accurate spectroscopic parameters, which serve as reliable starting values for extrapolation in higher frequency ranges and for the search of this sulfur-containing molecule in the interstellar medium.

Ion-dipole and ion-quadrupole interaction effects in ion-molecule reactions at collisional energies between 0 and 40·k_B K

V. Zhelyazkova[1], F. B. V. Martins[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich

Ion-molecule reactions are barrierless, exothermic reactions which proceed with high rate coefficients even at zero temperatures and are important for the synthesis of molecules in the interstellar medium [1]. These reactions are usually modelled by the classical Langevin model which predicts a temperature- and collisional-energy-independent reaction capture rate coefficients. However, at low collision energies, significant deviations from the Langevin rate coefficients arise resulting from the electrostatic interaction between the charge of the ion and the electric dipole [2-3] and quadrupole [4-5] moments of the neutral molecule.

We present experimental and theoretical studies of ion-molecule reactions involving He^+ and simple molecules. These reactions are studied within the orbit of a Rydberg electron in a merged Rydberg-neutral beams set-up as described in Refs.[2,4,6]. The helium atoms are excited to a low-field-seeking Rydberg-Stark state, and deflected and merged with the ground-state (GS) supersonic beam using a curved surface-electrode Rydberg-Stark decelerator [2]. We monitor the product-ion yield in a time-of-flight mass spectrometer as a function of the Rydberg helium velocity, while the GS beam velocity is kept constant.

The measured total product yields, I, display a significant dependence on the collision energy, E_{coll} , when the molecule has a permanent dipole or quadrupole moments. With decreasing E_{coll} , we observe (i) a significant increase of I in the case of a molecule with a permanent dipole moment (e.g., NH_3, ND_3 and CH_3F), and (ii) a pronounced suppression of I in the case of a molecule with a negative Q_{zz} component of the quadrupole moment (e.g., N_2 and CO). We calculate the reaction rate coefficients using an adiabatic capture model that includes the rotational-state-dependent energy shift of the molecule in the electric field of the He^+ ion and average over the rotational state population distribution in the supersonic source, including nuclear-spin statistics effects. The agreement between the experimental data and the model is very good for a number of molecules: CH_3F [2], NH_3, ND_3, N_2 and CO. The observed significant deviation from the Langevin model is attributed to the locking of the molecular angular momentum at low collisional energies [3].

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Absorption spectra of interstellar clouds

J. Krełowski[1]

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland

style="text-align: justify;">The interstellar space is filled with clouds of diffuse matter, forming the spectacular spiral arms of many galaxies, including our Milky Way system. Depending on the density, such clouds are usually divided into „diffuse", „translucent" (their presence revealed by absorption features, observed in the spectra of distant stars, shining through these clouds), „dense" and those which give births to new stars with their planetary systems. The lecture concerns physics and chemistry of the translucent clouds - which consist of several components: atomic gas, molecules, dust grains. In particular it addresses a scientifically very challenging issue of identifying (very likely molecular) carriers of the puzzling spectral features known as diffuse interstellar bands (DIBs) [1]. This set consists now more than 560 absorption features, lacking any identification [2]. They are believed to be carried by complex chemical species, including prebiotic ones, synthesized and preserved in translucent interstellar clouds. A vast majority of the interstellar absorptions are very shallow and thus an analysis of their profile shapes requires a very high resolution and S/N ratio. High precision DIB profiles may play a decisive role in the carrier's identification (it's 100 years after their discovery) since they are likely intrinsic to certain species. Translucent clouds are especially poorly understood. The abundances of about 10 identified molecular species, found in translucent clouds, are known for only a very limited number of clouds. It is reasonable to expect that an enormous size gap extending between the simplest two or three-atomic species (currently identified in translucent clouds) on one hand, and the dust grains (at least about 100 nm big - tens of millions atoms) on the other one, has to be bridged with medium or large-size molecules. The results, published during the last two decades, demonstrate red- and blue-shifts of some DIBs in relation to atomic lines as well as changes of their profiles which apparently vary from one to another specific environment. This was already supported by the finding of a relation between rotational temperatures of simplest carbon chains and profile shape of the 6196 DIB [3]. Any reliable chemical modelling of translucent clouds requires at least some selected physical parameters (like rotational temperature of the identified molecules or estimated UV flux) and the mutual abundance ratios for as many detected simple molecules as possible. The only way to identify the most likely molecular, carriers of DIBs is to compare laboratory spectra of suspect molecules with the observed DIBs. The laboratory spectra are expected to be determined in the Materials Spectroscopy Laboratory (FTS Bruker IFS-125HR) at University of Rzeszów, while the observational data – with the aid of the VLT ESO telescoped equipped with the high resolution, echelle spectrograph ESPRESSO – very recently commissioned – likely the worlds' best instrument of this kind.

Acknowledgements

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A Status Report on the Cologne Database for Molecular Spectroscopy, CDMS

H. S. Müller[1], P. Schilke[1], S. Schlemmer[1]

[1]I. Physikalisches Institut, Universität zu Köln

The CDMS[a] was founded more than 20 years ago to provide in its catalog section line lists of mostly molecular species which were or may be detected in space by radio astronomical means. The line lists are generated by fitting critically evaluated experimental data, mostly from laboratory spectroscopy, to established Hamiltonian models. The assessment of the experimental data and of the Hamiltonian model is very importantc and will be discussed in some detail. There are 1080 entries in the CDMS catalog as of mid-June 2021.

Other sections of the classical CDMS include a page on Molecules in Space and a help page for users of Pickett's SPFIT/SPCAT programs. There is also a VAMDC compatible incarnation of the CDMS which is linked to a plethora of other spectroscopic, collisional, and kinetic databases via the Vitual Atomic and Molecular Data Centre portal.[b]

A part of the contribution will deal with recent entries and with perspectives in relation to recent molecular line surveys. These include numerous diatomics, frequently containing metals, with highly excited states and isotopic species for several molecules already detected in space for the last project and excited states or isotopic species of known interstellar organic molecules, but also several new ones for the other projects.

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[a] Shortcut: cdms.de; web address: https://cdms.astro.uni-koeln.de/. The CDMS is supported by the Verbundforschung Physik of the BMBF (German Ministry of Science and Education), project ID 05A17PK1.

[b] http://www.vamdc.org/

Astrophysical High Resolution Mid-Infrared Observations - A Case Study of Late-type Stars

G. W. Fuchs[1], D. B. Witsch[1], E. Döring[1], T. F. Giesen[1], T. K. Greathouse[2], J. H. Lacy[3]

[1]Laboratory Astrophysics, Universtiy of Kassel, [2]Southwest Research Institute, Space Science Department, Texas, [3]Department of Astronomy, University of Texas at Austin

In the universe, chemistry starts when atoms are expelled from the hot inner regions of evolved stars and form molecules in the cooler outer atmospheres and stellar envelopes. Thus, at the end of their lifetime low and intermediate mass asymptotic giant branch (AGB) stars and the more massive red super giants, are building up strong stellar winds which are major sources of small to intermediate sized molecules and dust in the universe. Especially molecules composed of refractory materials like metal atoms, carbon or silicon are crucial for dust formation. To understand these formation processes these precursor molecules need to be observed and identified which can be done at infrared wavelengths using high resolution spectrographs. We have investigated the late type stars Canis Majoris, and o-ceti (Mira) using the TEXES spectrograph on the infrared telescope IRTF. The observations will be discussed and related to recent experimental investigations in our laboratory.

Differentiation of trapped Pyrene isomer cations by multiple photon dissociation

V. Mundlapati[1], A. Marciniak[1], A. BONNAMY[1], C. Joblin[1]*

[1]Institut de Recherche en Astrophysique et Planétologie (IRAP), Université Toulouse 3 – Paul Sabatier CNRS, CNES, 9 Avenue du Colonel Roche, F-31028 Toulouse, France

Polycyclic aromatic hydrocarbons (PAHs) are key species in both combustion processes and astrochemistry. They contain a large number of isomers that need to be characterized when studying chemical growth pathways and guiding astronomical search. In this work, we report experiments using multiple photon dissociation (MPD) spectroscopy in the PIRENEA setup[1] on trapped PAH isomers of m/z=202, namely pyrene (Pyr^+), fluoranthene (Flu^+), and 9-ethynylphenathrene (EtP^+) cations. We recorded the dissociation yields of the parent cations as a function of the laser pulse energy and at different wavelengths, which were selected from their MPD action spectra. When exciting in the strong band of Pyr^+ at 436 nm, we found that the fitted linear function curve of Flu^+ was far from the other two isomers, Pyr^+ and EtP^+, as shown in Fig. 1. In a spectral range of weaker absorptivity (here 455 nm), we found that the three isomers can be well separated from each other, as shown in Fig. 1. We also recorded the dissociation yields as a function of the number of laser pulses. In this case, we could differentiate the three isomers by their major fragments, H-loss and $2H(H_2)$-loss channels, upon excitation at 436 nm using small and high laser pulse energies.

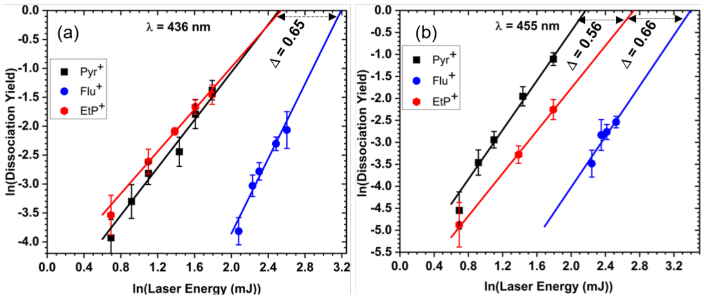

Figure 1: Dissociation yields of m/z=202 isomer cations as a function of the laser pulse energy at (a) 436 nm and (b) 455 nm excitation energies.

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Precision infrared spectroscopy using a fibre link for the distribution of the Swiss primary frequency standard

A. Shlykov[1], M. Roguski[1], M. Sinhal[1], Z. Meir[1], M. Bertrand[2], J. Faist[2], F. Merkt[3], E. Heiri[4], D. Husmann[5], J. Morel[5]*, S. Willitsch[1]*

[1]University of Basel, Department of Chemistry, [2]ETH Zürich, Institute for Quantum Electronics, [3] ETH Zürich, Laboratory of Physical Chemistry, [4]SWITCH, [5]Swiss Federal Institute of Metrology METAS

Trapped atoms and atomic ions are among the best-controlled quantum systems which have found widespread applications in quantum science. However, the same degree of control over molecules has so far been challenging to achieve due to their complex energy-level structure. We overcome this problem by employing a high-fidelity quantum-state detection protocol that uses a single co-trapped atomic ion as a probe for the molecular state [1]. This protocol allows us to perform highly sensitive and precise spectroscopic experiments on dipole-forbidden infrared transitions in N_2^+ driven by a quantum cascade laser. The absolute frequency stability of the measurements is provided by referencing all laser frequencies to the Swiss primary frequency standard, the Cs atomic fountain clock FoCS-2, operated by the Swiss Federal Institute of Metrology METAS in Bern [2]. The present approach paves a way for establishing new methods for precision spectroscopic measurements in the infrared domain, for new frequency standards in this regime, for new ways of investigating the state-to-state dynamics of chemical reactions, and for probing spectroscopically fundamental physical questions such as temporal variation of fundamental constants.

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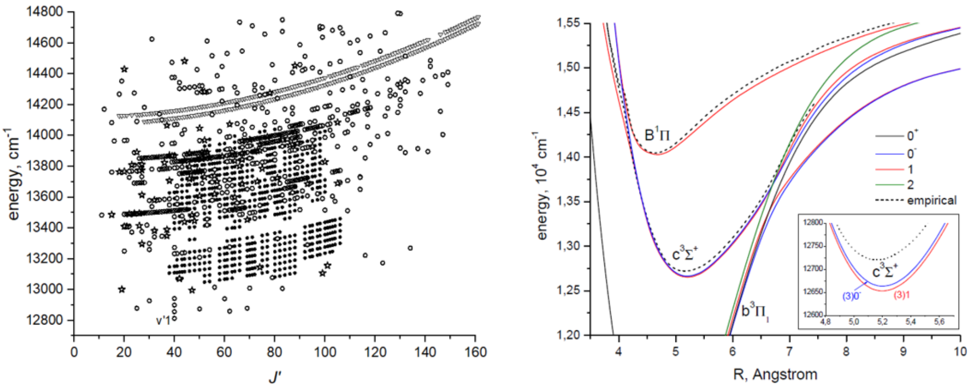
High Resolution Spectroscopy and Potential Reconstruction of the $c^3\Sigma^+(\Omega = 1)$ State in KCs

R. Ferber[1], V. Krumins[1], A. Kruzins[1], M. Tamanis[1], A. V. Oleynichenko[2,3], A. Zaitsevskii[2,3], E. A. Pazyuk[3], A. V. Stolyarov[3]*

[1]Laser Center, Faculty of Physics, Mathematics and Optometry, University of Latvia, [2]Petersburg Nuclear Physics Institute , [3]Department of Chemistry, Moscow State University

We report on Fourier-transform (FT) spectroscopy measurements and electronic structure calculations on the $c^3\Sigma^+$ state of KCs. The laser-induced fluorescence (LIF) spectra of the $c^3\Sigma^+ \to a^3\Sigma^+$ transition were recorded with FT spectrometer IFS125-HR (Bruker) within 9000 to 10000 cm^{-1} range. The Ti:Saphire laser Equinox/SolsTis (MSquared) operated within 13800 - 12200 cm^{-1} range was exploited. Comparison of measured LIF intensity distribution with the calculated one unambiguously confirms the vibrational numbering suggested in [1]. About 800 rovibronic term values belonging to both *e/f* components of the $c^3\Sigma^+$ state, covering vibrational levels from $v = 0$ to more than 40 and rotational levels from $J = 11$ to 149 were determined (Figure, left panel), with absolute accuracy about 0.01 cm^{-1}. Experimental term values up to $v = 22$, supplemented by the respective term values from [1], were involved in a direct point-wise potential fit of the $c^3\Sigma^+$ ($\Omega = 1^{\pm}$) state; Ω-doubling due to spin-rotational interaction with the $c^3\Sigma^+$ ($\Omega = 0^-$) state was taken into account. The analysis was greatly facilitated by the Fock space relativistic coupled cluster (FS RCC) of the potential energy curves for the $B^1\Pi$, $c^3\Sigma^+$, and $b^3\Pi$ states (Figure, right panel), as well as of the spin-forbidden *c* – *X* and spin-allowed *c* – *a* transition dipole moments. The constructed potential allows to reproduce the present measured experimental term values within the accuracy of about 0.015 cm^{-1}.



Figure, left panel: KCs $c^3\Sigma^+$ state term values as dependent on rotational quantum number *J'*, empty circles – *e* levels, asterisk – *f* levels, points – data from [1], triangles– $B^1\Pi$ state data [2]; right panel: potential energy curves for the $B^1\Pi \sim b^3\Pi \sim c(2)^3\Sigma^+$ complex in KCs calculated within the FS-RCC approach compared to empirical curves (dotted lines) for $c(2)^3\Sigma^+$ [1] and $B^1\Pi$ [2].

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CO-Ar collisions: Experimental spectra and theoretical model agree at sub-percent level at pressures varying within four orders of magnitude

N. Stolarczyk[1], E. A. Serov[2], D. S. Makarov[2], I. N. Vilkov[2], . Y. Golubiatnikov[2], A. A. Balashov[2], M. A. Koshelev[2], P. J. Wcisło[1], F. Thibault[3]*, M. Y. Tretyakov[2]*

[1]Nicolaus Copernicus University, Faculty of Physics, Astronomy and Informatics, Toruń, Poland, [2] Institute of Applied Physics of the Russian Academy of Sciences, [3]Univ Rennes, CNRS, IPR (Institut de Physique de Rennes), Rennes, France

CO-Ar molecular system is a prototype of atmospherically relevant cases. It is, on the one hand, affordable for calculation of the line shape parameters by modern *ab initio* methods [1,2], and, on the other hand, is very convenient for experimental studies because of its regular, well spaced rotational spectrum having a moderate intensity [1]. The shapes of molecular optical resonances are strongly dependent on pressure. To test that our quantum-scattering calculations are valid in a broad pressure range, we performed our spectroscopic study of the CO-Ar collisional system at pressures spanning four orders of magnitude.

Three independent spectroscopic techniques [4,5,6] were used to record the spectral line shape of the first rotational overtone of the CO molecule preturbed by Ar. Simultaneously we performed fully *ab initio* quantum scattering calculations on two recent potential energy surfaces [1,7]. We employed the sophisticated spectral line-shape model to simulate the shapes of the molecular optical resonance.

We show that the simulated collision-perturbed spectra, which are based on our fully *ab initio* calculations, agree with the experimental line profiles at sub-percent level over a wide range (more than four orders of magnitude) of pressures. We demonstrate that the agreement between theory and experiment can be further improved if the model accounts for the collisional transfer of an optical coherence between different rotational transitions (the line-mixing effect). We show that the two surfaces tested in this work lead to a very similar agreement with the experiment. Capability of calculating line shape parameters in a broad range of temperatures is therefore demonstrated.

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Gas-phase spectroscopy of photostable PAH ions from the mid- to far-infrared

S. D. Wiersma[1,2], A. Candian[1], J. M. Bakker[2], A. Petrignani[1]*

[1]Van `t Hoff Institute for Molecular Sciences, University of Amsterdam, PO Box 94157, 1090 GD, Amsterdam, The Netherlands, [2]Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

We present high-sensitivity, gas-phase infrared multiple photon dissociation (IRMPD) spectra of the three cationic polycyclic aromatic hydrocarbons (PAHs) — phenanthrene, pyrene, and perylene — employing a 7-T Fourier-Transform Ion Cyclotron Resonance mass spectrometer, integrated in the Free-Electron Laser for Intracavity Experiments FELICE. The intracavity configuration can provide such high photon densities that the IRMPD spectra of these strongly-bound, photo-resistant PAHs can be recorded over the 100-1700 cm^{-1} (6–95 μm) spectral range, with a sensitivity that allows for the detection of combination modes with predicted intensities as low as 0.01 $km \cdot mol^{-1}$ near 400 cm^{-1} (25 μm). Both harmonic and anharmonic spectra were calculated with Density Functional Theory, at the B3LYP/6-311++G(2d,p) and the B3LYP/N07D level respectively. The investigated spectral range covers both local vibrational modes involving C–C and C–H bonds in the mid-IR, and large-amplitude skeletal modes in the far-IR, both of which match the IRMPD spectra well. All currently available IRMPD spectra for PAH cations were superimposed over previously predicted theoretical trends for far-IR vibrational modes depending on PAH shape and size from the NASA Ames PAH IR Spectroscopic Database [1,2], and only a relatively small redshift was found compared to theory (6–11 cm^{-1}). We conclude that the absence of spectral congestion and drastically lowered anharmonic redshift (compared to the mid-IR) could make the measured wavelengths in the far-IR a viable candidate for theoretical benchmarking, which can aid in the search for individual large PAHs in the interstellar medium.

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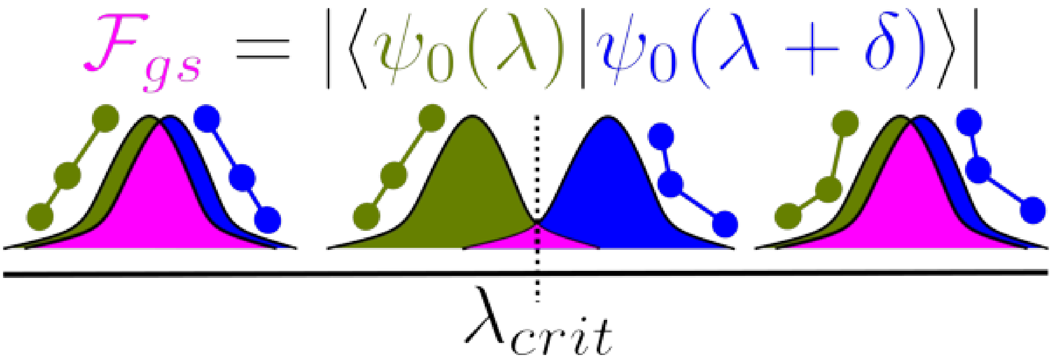
Effects of Excited State Quantum Phase Transitions over the Fidelity Susceptibility in the 2D Limit of the Vibron Model: Application to Molecular Bending Spectra

J. Khalouf-Rivera[1], M. Carvajal[1]

[1]University of Huelva

Molecular bending spectra can be broadly categorized into three physical cases, depending on the molecular equilibrium configuration: linear, bent, and nonrigid. We have studied the three cases in detail with an extended Hamiltonian (including up to four-body interactions) of the 2D limit of the Vibron Model (2DVM). We have obtained bending band origin predictions within experimental accuracy as well as the corresponding eigenstates for several molecules [1].



The particular spectroscopic signatures characterizing states that straddle the barrier to linearity in nonrigid molecules have been pinpointed with the quantum monodromy and the Birge-Sponer plots. In addition, we propose a characterization of the obtained bending eigenstates making use of the Quantum Fidelity Susceptibility [2]. This quantity allows us to determine in an elegant and basis-independent way the linear or bent character of any excited state.

As an application, we have studied, using the above mentioned quantities, the bending spectra of several molecules of interest in different fields: HNC, OCCCO, CH_3NCO, ClCNO, NCNCS, and Si_2C [1-3].

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Photodissociation of exoplanetary important diatomic molecules

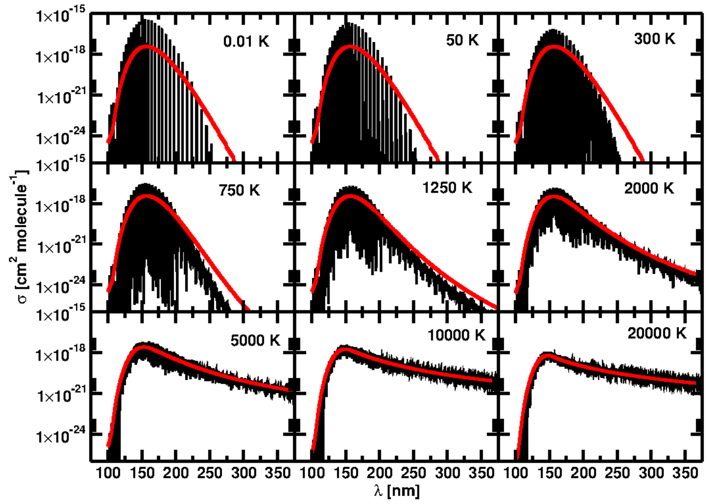
M. Pezzella [1], S. N. Yurchenko [1], J. Tennyson[1]*

[1] UCL Department of Physics and Astronomy ,University College, Gower St, London WC1E 6BT

The destruction of molecules by photodissociation influences the composition and dynamics of exoplanets, particularly in the presence of a UV-rich stellar environments, where molecules are hot. Current photodissociation calculations generally assume *T*= 0 K, appropriate for the cold interstellar medium but inadequate for hot (exo)planets and stars.

We compute temperature-dependent photodissociation cross sections for molecules found in these atmospheres. The cross sections are calculated by solving the nuclear-motion Schrödinger equation as part of the ExoMol project using codes Duo and Exocross,[1,2] and averaging results obtained as discrete spectra.

We benchmark our results for different systems. The general validity of the methodology is tested considering the $A^1\Pi$ <-$X^1\Sigma^+$ transition of HCl at different *T*. Our cross sections and rates agree with published results[3](2.31*10^{-10} s^{-1} versus 2.10*10^{-10} s^{-1} respectively). The photodissociation spectrum of NaCl varies consistently with *T*: at *T*=100 K, there two peaks at 240 nm and 260 nm; while at *T*=1500 K the peaks merge. Preliminary data from AlH are presented as well.



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An open-source Python library for calculating energy levels and spectra of diatomic molecules

I. Havalyova[1], A. Pashov[1]

[1]Faculty of Physics, Sofia University, 5 James Bourchier Boulevard, 1164 Sofia, Bulgaria

We developed an open-source package for performing computations of diatomic energy levels and spectra. In particular, by solving directly the radial Schrodinger equations it allows to compute eigenvalues and eigenvectors for a system of an arbitrary number of coupled electronic states. The system is defined by potential energy curves and the radial part of the corresponding coupling operators. It supports a large number of rotational and relativistic Hund's case (a) operators. The spectral line positions and line intensities can also be calculated. Another important feature is the ability to optimize the parametrized electronic potential energy and coupling functions by fitting the computed energy levels to experimental data. It follows an object-oriented approach with easy-to-use functionality and a user-friendly interface. The implemented numerical routines are efficiently vectorized.

High-Resolution far infrared spectroscopy and analyses of trioxane

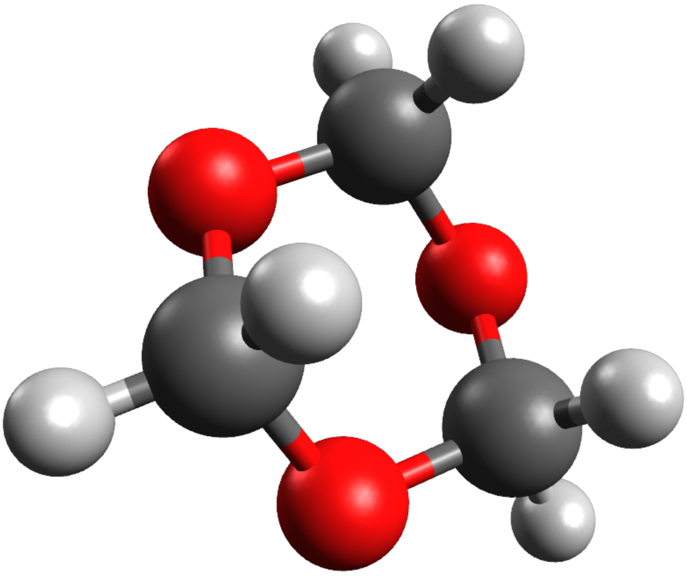
C. Richard[1], V. Boudon[2], P. ASSELIN[3], O. Pirali[4]

[1]CNRS / Université Bourgogne Franche-Comté, [2]Laboratoire Interdisciplinaire Carnot de Bourgogne, [3]Laboratory MONARIS UMR 8233 CNRS, Sorbonne Univers, [4]Institut des Sciences Moleculaires d'Orsay

Trioxane, $(H_2CO)_3$, is a symmetric top that belongs to the C_{3v} symmetry group. The molecule owns 20 fundamental modes that are dispatched as 7 symmetric vibrations of type A1, 3 vibrations of type A2 and 10 doubly degenerate vibrations of type E.

Infrared spectra of trioxane have been recorded in the 50-650 cm^{-1} range using a high resolution Bruker IFS 125 interferometer located at the AILES beamline of the SOLEIL synchrotron facility. Owing to its higher brilliance in the far-infrared region, the SOLEIL synchrotron radiation was used to improve the signal-to-noise ratio of the spectrum at the maximal resolution of 0.001 cm^{-1}.

We present here a detailed analysis and modeling of intense OCO deformation ν_7 and ν_{19} modes as well as weaker weaker CH_2 torsion ν_{20} mode and its first overtone $2\nu_{20}$. Thanks to the formalism and programs developed in Dijon, we could determine accurately the effective Hamiltonian parameters for these 3 modes.



The role of solvent interactions in the catalysis of the bio-renewable chemical, 6-amyl-α-pyrone, investigated using rotational spectroscopy.

H. Singh[1,4], M. Fatima[2], M. A. Haider[3], M. Schnell[1,4]*

[1] Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany, [2]I. Physikalisches Institut, Universität zu Köln, Köln, Germany, [3]Indian Institute of Technology Delhi, Delhi, India, [4]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Kiel, Germany

Lignocellulosic biomasses are often reacted on catalysts in solvents to produce high-value chemicals [1]. One such example is the catalytic transfer hydrogenation (CTH) of 6-amyl-α-pyrone (6PP), a biomass platform chemical, producing δ-decalactone (DDL), that is used as an aroma compound. The CTH reaction carried out in different solvents under similar conditions is reported to produce significant variation in 6PP conversion and DDL yield varying from 6 % to 79 % [2]. These variations in yield during CTH can be attributed to numerous reasons, such as dispersive interactions during micro-solvation of 6PP.

To understand the role of dispersion interactions in these reactions, we employ high-resolution chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy under the isolated conditions of a molecular jet in the gas phase. This technique can accurately reveal the structures and internal dynamics of molecules and weakly bound complexes at the molecular level. We first investigate the effect of intramolecular interactions within 6PP ($C_{10}H_{14}O_2$) in the 2-8 GHz frequency range. Due to the flexibility of the pentyl chain within 6PP, a conformational search revealed more than 20 different conformers within a relative energy of less than 6 kJ/mol. The optimized structures are good starting points for the analysis of the rotational spectra. We will present the experimental results that will allow us to understand the role of intramolecular interactions for the observed structures of the monomer. This study will then be the basis for investigating the micro-solvation of 6PP with solvents such as methanol, cyclohexane, and tetrahydrofuran.

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Differentiation of Pyrene$^+$ isomers by low energy collision induced dissociation

V. Meloottayil[1], H. Sabbah[1], C. Joblin[1]*

[1]3. Institut de Recherche en Astrophysique et Plan´etologie (IRAP), Universit´e toulouse III- Pual Sebatier CNRS, CNES, 9 Avenue du Colonel Roche, F-31028 Toulouse, France

Polycyclic aromatic hydrocarbons (PAHs) are important species in environmental science and astrochemistry. They contain a large number of isomers and specific information on their structure is needed to explain PAH toxicity and understand chemical growth pathways. Chromatography is an efficient tool to characterize PAH isomers when the samples are solvable and sufficient in quantity. In this work and in a companion work[1], we investigate methods to differentiate isomers of PAH cations, which are trapped after their production in the gas phase by laser desorption ionization (LDI). We focus here on collision induced dissociation (CID) involving low-energy collisions with a rare gas, whereas photo-excitation is reported in ref. 1. Pyle et al[2] showed that nonresonant multistage CID can be used as a mean to separate isomers, though the reproducibility of their data was limited. We used the AROMA setup[3] to perform CID experiment on pyrene cation ($C_{16}H_{10}^+$, m/z=202) and some of its isomers, fluoranthene and 9-ethynylphenanthrene. In this experiment, gas phase ions produced by a two-step LDI are injected into a quadrupole ion trap where they are kinetically excited by a dipolar field at a frequency close to the resonant frequency (187 kHz) of m/z=202 and with an amplitude of 260 mV. The excitation is performed in the presence of a buffer gas (He or Ar), which leads to collisional activation of the ions. CID of each isomer was studied under two activation conditions (see Fig. 1). We recorded the breakdown curves as well as the H and 2H (or H_2) loss curves of the three isomers. We observed differences between isomers both in the breakdown curves and in the 2H (H_2) / H loss ratio. This analysis provides insights into the competition between H_2 and sequential H production in the different isomers. As reported earlier[2], the trapping stability appears as a limiting factor to apply this method on a complex mixture.

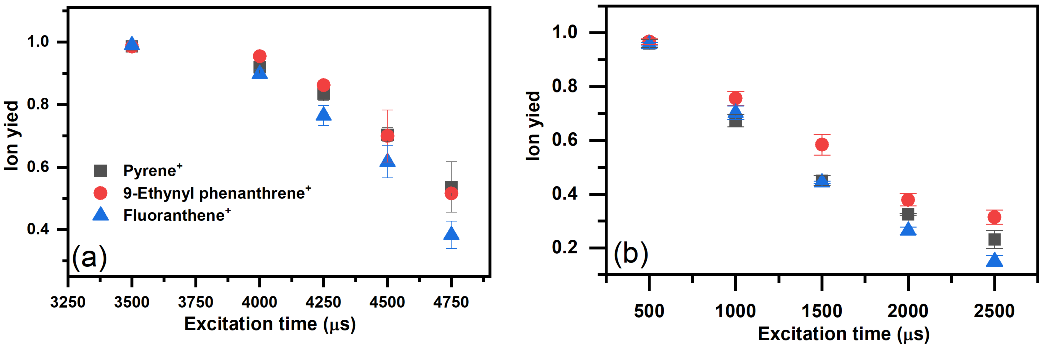

Figure 1. CID breakdown curves of $C_{16}H_{10}^+$ isomers, obtained as a function of dipolar excitation (DE) excitation time. The experiments were carried out at a fixed DE amplitude of 260mV using (a) on resonance excitation in the presence of He and (b) off resonance excitation in the presence of Ar collisional gas.

Acknowledgement: The research leading to these results has received funding from the European Research Council under the European Union's Seventh FrameworkProgramme (FP/2007-2013) ERC-2013-SyG, Grant agreement Nà 610256 NANOCOSMOS.

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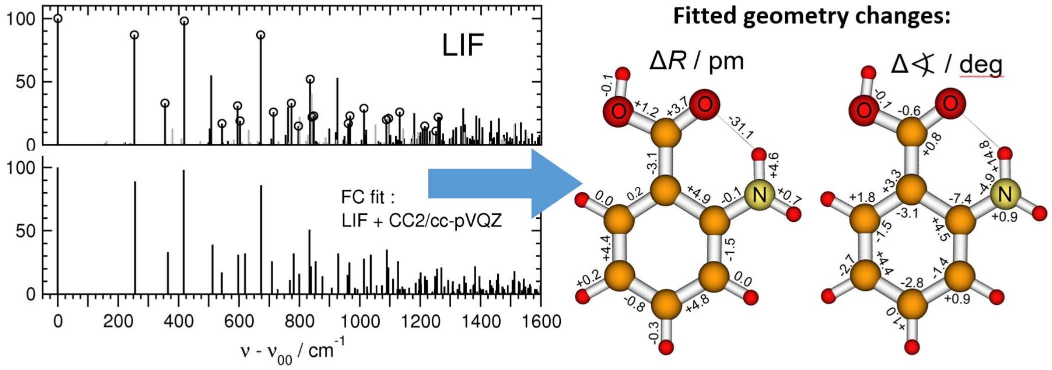
Structural implications of LIF spectroscopy and Franck-Condon modelling for intramolecular hydrogen bonding in the $S_1(\pi\pi^*)$ excited state of anthranilic acid

P. Kolek[1], M. Andrzejak[2], J. Goclon[3], W. Szajna[1], I. Piotrowska[1], S. Ryzner[1], R. Hakalla[1]*

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland, [2]K. Gumiński Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Kraków, Poland, [3]Institute of Chemistry, University of Bialystok, Poland

Experimentally-based estimation of the changes in equilibrium geometry upon the $S_0 \rightarrow S_1(\pi\pi^*)$ excitation via fitting of Franck-Condon factors is tested for reliability. The modelling is based on the experimental intensities in the LIF excitation spectrum of jet-cooled molecules[1]. Band intensities are transformed into geometry changes with the aid of the vibrational modes computed using the CC2 method[2] (the perturbative approximation to CCSD coupled-cluster), as well as with TDDFT(B3LYP)[2].



An interesting effect of the excitation in anthranilic acid is a significant dislocation of hydrogen atom, often viewed as the excited-state intramolecular proton transfer ESIPT. The LIF+CC2 Franck-Condon fitting predicts a dramatic shortening of the O⋯H distance by 31±1.5pm, from 1.91Å in the ground state to 1.60Å in the excited state[3]. The changes in bond alternation within the benzene ring and in the H-chelate ring (approaching 5pm according to the LIF+CC2 fit) and the shortening of the O⋯H bond are up to 1pm larger than modelled with the LIF+TDDFT fit. The largest deformation of valence angles concerns the C2–C1–N angle and approaches 7.5°. It is imposed by the shorteninig of the intramolecular hydrogen bond. The magnitude of the substantial changes in valence angles reaches typically 5° and are larger by 0.5°-1.0° according to LIF+CC2 FC fit than the LIF+DFT fit.

Thus, the essential discrepancies of the ab initio predicted shortening of the O⋯H distance (varying from 14.6pm[1] with Hartree-Fock and CIS methods, through 19.1-22.6pm[2] using TDDFT with a series of basis sets, up to 27.3-28.6pm[2] with CC2), have been corrected via the Franck-Condon fitting to the experimetal band intensities in the LIF spectrum. Obtaining the consistent evaluation of geometry changes[3] is an important achievement of the fitting of FC factors to the experimental band intensities in the LIF spectrum.

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High-resolution FTIR infrared absorption cross sections of 1-^{13}C propane ($^{13}CH_3CH_2CH_3$) and natural propane from 3 µm to 14 µm at 296 K and 250 K

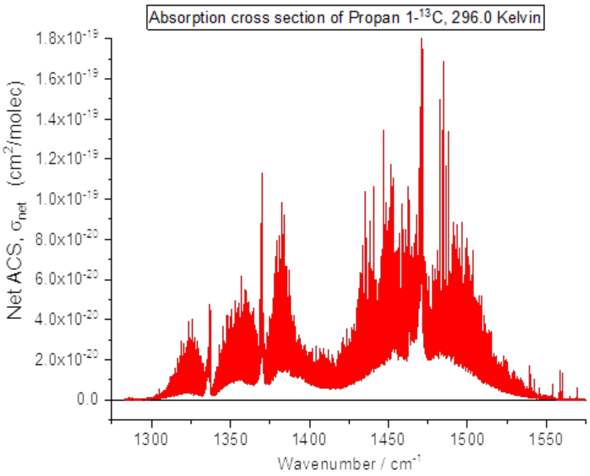
G. Li[1], A. Nataraj[2], J. Mohn[2], M. Kim[1], L. Emmenegger[2], V. Ebert[1]*

[1]PTB, Bundesallee 100, 38116 Braunschweig, [2]Empa, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

Organic molecules like hydrocarbons are key to the Earth-life system. Recent technological advances in high-sensitivity isotope ratio analysers using powerful lasers in the mid-infrared region (MIR) [1] unlock the potential of isotope analysis beyond simple methane. 1-^{13}C propane is a new environmental and biological tracer, which provides new opportunities and angles to answer questions related to Earth and Planetary sciences [2].

Here, we report absorption cross-sections of pure 1-^{13}C propane in the spectral region from 3 µm to 14 µm at resolutions from 0.003 cm^{-1} to 0.0056 cm^{-1} and at two temperatures around 296 K and 250 K using a Bruker IFS125HR spectrometer. The dataset is useful for the line selection in highly sensitive MIR spectrometry of 1-^{13}C propane at ambient level in the field, as well as for carbon-isotope analysis of propane in the laboratory. To facilitate this, we also measured natural propane at the same conditions. The results are compared to respective spectra in literature [3-5] and from the Pacific Northwest National Laboratory (PNNL).

The project EUMETRISPEC [6] has received funding from the EMRP programme. This work is also linked to the STELLAR project (19ENV05) [7] and SIRS project (16ENV06) [8] which have received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.



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Metrology compatible CO_2, N_2, CH_4, Ar, O_2 and air broadening coefficients of HCl in the 1-0 band

J. A. Nwaboh[1], Z. Qu[1], G. Li[1], O. Werhahn[1], V. Ebert[1,2]

[1]Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, [2]Technical University of Darmstadt, Department of Mechanical Engineering, Reactive Flows and Diag-nostics, Otto-Berndt-Str. 3, 64287 Darmstadt, Germany

style="text-align: justify;">Hydrogen chloride (HCl) is a common and important molecule that has been studied in a variety of applications such as clean room environments, biomethane conformity assessments, industrial emissions monitoring, and atmospheric sciences [1-4]. For spectroscopic measurements, we present measured collisional broadening coefficients of HCl lines in the 1-0 band. Focus was placed here on the consistency and data quality (traceability of the results to the international system of units - SI and Guide to the expression of uncertainty in measurement - GUM [5] compliant uncertainty assessment) of the measured CO_2, N_2, CH_4, Ar, O_2, and air -induced broadening coefficients of the P(6)-HCl line (also P(5)-HCl line [4]). Mid-infrared spectrometers have been developed to perform the measurements. Beside other applications, the measured collisional broadening coefficients can be used for line shape modelling of the super-Lorentzian effect [6]. The measured broadening coefficients are compared to data in literature. Our measurements were performed in the pressure range between 0 – 1000 hPa at a typical interval of 100 hPa, which is complementary to much higher pressures adopted (up to 5 MPa) in interesting previous works [6]. Ultimately, improved combined uncertainties in the 1 - 3 % range have been achieved in our study while addressing SI-traceability of the results.

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Diatomic Molecules in Sunpots

S. T. Donnelly[1], M. Gorman[1], J. Tennyson[2], S. Yurchenko [2]

[1]Aberystwyth University, Department of Physics, [2] UCL Department of Physics and Astronomy

Since the 1930’s it has been known that sunspots are cool enough to allow for the formation of diatomic molecules. Early work by Richardson[1] and Babcock[2] inspired W¨ohl[3] to investigate the existence of diatomic molecules in the umbrae of sunspots, investigating the existence of 41 molecules and using a method based on wavelength coincidence on experimental rotational line intensity.

We have been generating computational linelists for SrH and BaH which are of interest in sunspot umbrae. Ab-initio calculations were undertaken in MOLPRO[4] at the MRCI level, covering the 8 lowest-lying electronic states. Calculations were then refined using experimental spectroscopic data. The aug-cc-pV5Z-PP basis sets developed by the Hill group[5]have been used with the Stuttgart effective core potentials[6] for the 28 and 46 core electrons of Sr and Ba respectively. All electrons outside of the core were fully correlated using an active space of A1=8, B1=3, B2=3, A2=1 within the C2V framework for both SrH and BaH. This active space covers the four lowest dissociation limits for the molecules. Spin-orbit calculations have been completed for these low-lying states. Ground state Re’s for SrH and BaH are 2.1490 ˚A and 2.2312 ˚A respectively; comparing favourably with experimental values of 2.1461˚A for SrH [7], and 2.2318˚A for BaH[8]. Dissociation limits for the groundstates of SrH and BaH are calculated to be 14123.3313 cm−1[9] and 16916.0667 cm−1[10] respectively, agreeing with previous ab-intio calculations conducted.

At present linelists for the X2Σ+states for SrH and BaH have been completed to an accuracy on the order of 0.1 cm−1 (1 part in 10^4) or better. Currently, work is progressing to include 3 low-lying electronic states for SrH and 4 low-lying states for BaH. The vibrational and rotational coverage varies by state, but are within the region of V=25 and J=65.5, far exceeding existing experimentally measured transitions. The final linelists will be computed for all major isotopologues of the SrH and BaH molecules including the deuterium counterparts.

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The spectrum of ammonia near 0.793 µm

N. F. Zobov[1], T. Bertin[2], J. Vander Auwera[2], S. Civis[3], A. Knızek[3], M. Ferus[3], R. I. Ovsyannikov [1], V. Y. Makhnev[1], J. Tennyson[4], O. L. Polyansky[1]*

[1]Ulyanov Street 46, Nizhny Novgorod, Russia 603950, [2]SQUARES, C.P. 160/09, Université Libre de Bruxelle, [3]Czech Academy of Science, Dolejskova 2155/3, Prague 18223, Czech Republic, [4] Department of Physics and Astronomy, Gower Street, London WC1E 6BT, United Kingdom

Two sets of NH3 absorption spectra covering the 0.793 µm region are recorded using two Bruker IFS 125 HR Fourier transform spectrometers. Three unapodized absorption spectra are recorded in Brussels over the range 11000 − 14500 cm^{-1} and the positions and intensities of 1114 ammonia lines observed in the 12491 − 12810 cm^{-1} region are measured. 367 additional lines are identified in an ammonia absorption spectrum recorded in two steps in Prague, using two different interference filters covering the 12000 − 12500 and 12400 − 13000 cm^{-1} ranges. The 1481 measured ammonia lines are analyzed using an empirical line list computed using variational nuclear motion calculations [1] and ground state combination differences. Transitions are assigned to vibrational states with $4\nu_{NH}$ stretching excitation ($v_1 + v_3 = 4$). 278 out of the 1481 measured lines are assigned to 300 transitions and 119 upper state energy levels are derived from the frequencies of the assigned transitions.

This work was supported by the ERC Advanced Investigator Project 883830, the UK Natural Environment Research Council grant NE/T000767/1 and the Russian Fund for Fundamental Studies. RIO, VYuM, NFZ and OLP acknowledge support by State Project IAP RAS No. 0035-2019-0016. The work carried out in Prague is part of a research series funded by grant no. 19-03314S of the Czech Science Foundation and ERDF/ESF “Centre of Advanced Applied Sciences” (No. CZ.02.1.01/0.0/0.0/16 019/0000778).

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Millimetre-wave rotational spectrum of iminopyruvonitrile in its ground state and vibrationally excited states

K. Luková[1], L. Kolesniková[1], J. Koucký[1], K. Vávra[1], P. Kania[1], J. C. Guillemin[2], Š. Urban[1]*

[1]University of Chemistry and Technology, Department of Analytical Chemistry, Technická 5, 166 28 Prague 6, Czech Republic, [2]UMR 6226 CNRS – ENSCR, Institut des Sciences Chimiques de Rennes, Rennes, France

Up to now, more than 200 molecules have been identified in the interstellar medium, with nitriles being the most abundant of nitrogen-bearing molecules [1]. Here we present precise laboratory measurements of rotational spectra of iminopyruvonitrile (IPN, 2-iminopropane nitrile), a methyl derivative of in the ISM previously identified 2-iminoethane nitrile [2].

High-resolution rotational spectrum of IPN was recorded in different frequency regions from 125 to 330 GHz using the Prague millimetre wave absorption spectrometer [3]. The splitting arising from the internal rotation of the methyl group was assigned and analysed employing the programs XIAM [4] and ERHAM [5]. The refined set of molecular parameters including the barrier of internal rotation was obtained for the most stable conformer of IPN upon existing rotational study results by Groner et al. [6]. In addition, the transitions of the low-lying vibrationally excited states were also observed and assigned, aided by the theoretical predictions performed by MP2 and DFT computational methods.

The funding from the Czech Science Foundation (GACR, grants 19-25116Y and 18-08667S) is gratefully acknowledged.

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High-resolution spectroscopic study of N_2O^+

A. Roucou[1], X. Urbain[1], C. Lauzin[1]*

[1]Institute of Condensed Matter and Nanosciences, UCLouvain

The photodissociation spectra of N_2O^+ have been measured in the UV range using the new STARGATE instrument (Spectroscopy of Transient Anions and Radicals by Gated and Accelerated Time-of-flight Experiment) developed in UCLouvain [1]. This poster will present the rovibronic analysis of the $A^2\Sigma^+(002) \leftarrow X^2\Pi(000)$, $A^2\Sigma^+(101) \leftarrow X^2\Pi(000)$ and $A^2\Sigma^+(003) \leftarrow X^2\Pi(000)$ bands measured at 550 K between 30500 and 32500 cm^{-1}. Those spectra were recorded by monitoring the formation of NO^+ as function of the laser frequency. A global vibronic fit including these bands, Q-branch head of overtones, both observed for the first time, combination bands and the relevant data from the literature has been performed. This global fit, its performances and the inclusion of the Renner-Teller effect involving the $X^2\Pi$ and $A^2\Sigma^+$ states will also be detailed.

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Continuum absorption by pure CO_2 and CO_2-Ar mixture at millimeter waves: Meticulous measurements and classical trajectory-based simulation

T. A. Odintsova[1], E. A. Serov[1], A. A. Simonova[2], M. Tretyakov[1], A. A. Finenko[3], S. E. Lokshtanov[3], S. V. Petrov[3], A. A. Vigasin[4]

[1]Institute of Applied Physics of RAS, Nizhniy Novgorod, Russia, [2]V.E. Zuev Institute of Atmospheric Optics SB RAS, Tomsk, Russia, [3]Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia, [4]Obukhov Institute of Atmospheric Physics, RAS, Moscow, Russia

We acknowledge full co-authorship of A. A. Balashov, M. A. Koshelev and A. O. Koroleva from Institute of Applied Physics RAS, Nizhny Novgorod, Russia.

This study of the millimeter wave continuum absorption in the CO_2-X (X=Ar, CO_2) mixtures was, in particular, inspired by the success of the classical trajectory-based formalism recently developed to simulate collision-induced absorption (CIA) spectra [1-3]. On the one hand, the agreement, once achieved, between experimental data and the calculated results promotes a better understanding of the nature of the continuum on a much broader scale. On the other hand, the knowledge of the CO_2 continuum is required to model the radiative processes in the CO_2-rich planetary atmospheres, such as those of Venus and Mars.

Experimental spectra of continuum absorption in pure CO_2 and a mixture of CO_2 with Ar were recorded at room temperature and pressures up to 2 atm using a resonator spectrometer [4]. Measurements covered 105-240 GHz range allowing determining frequency dependence of the continuum absorption.

The agreement between the measured and trajectory-based data supports the reliability of both our experimental and theoretical methods. Previously available experimental data on the CO_2-X millimeter wave continuum were obtained on a rare frequency grid and, in general, are characterized by unsatisfactory accuracy. Classical trajectory-based formalism made it possible to examine the variation of the far-infrared/mw spectral profile of CO_2-Ar dimer as a function of temperature. The structureless pedestal of the CIA profile corresponding to free/quasibound pairs states is supplemented by the weak signatures of intermolecular vibrational bands of true dimers. Conspicuous fingerprints of intermolecular vibrational bands are seen at extremely low temperatures, which transform to the CIA-like, virtually structureless envelope as the temperature of the simulation increases.

This work was partially supported by RFBR projects No. 18-55-16006.

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Spectroscopic Measurements of Ion-pair States of Polyatomic Molecules

C. Kreis[1], U. Hollenstein[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich

v class="ab-texts">
We present the results of spectroscopic investigations of ion-pair states of small polyatomic molecules. Ion-pair states of diatomic molecules are well characterized [1,2].
However, only few studies of ion-pair states of polyatomic molecules have been conducted [3,4] and many of their characteristics are not well understood.
Accurate threshold energies give access to thermochemical properties like the bond energy. We are currently investigating triatomic systems in particular H_2S and its isotopomers.
The molecule of interest in its gas phase is cooled down in a supersonic expansion. The cold gas cloud passes a skimmer before it is excited via a one-photon transition with narrow-band VUV laser radiation and extracted in a photoion/photoelectron time-of-flight spectrometer.
The threshold of the formation of ion-pair states is determined and spectra of vibrational ion-pair states presented.

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H_2O absorption line parameters in the 5900–6100 cm^{-1} spectral region

T. Petrova[1], V. Deichuli[1], A. Solodov[2], T. Chesnokova[2], A. Trifonova-Yakovleva[2]

[1]V.E. Zuev Institute of Atmospheric Optics, Siberia, [2]V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev sq.,634055, Tomsk, Russia

The H_2O absorption lines broadened by air pressure were recorded using Fourier spectrometer Bruker IFS 125 HR in the 5900-6100 cm^{-1} spectral region. The intensities, broadening and shift coefficients of H_2O absorption lines were retrieved for Voigt profile and ones taking into account a dependence of the broadening on collision molecules speed (qSDV). The intensities calculated in this work for qSDV are compared with the values taken from the HITRAN spectroscopic database.

The atmospheric transmission was calculated with use of H_2O line parameters from various versions of the HITRAN and GEISA spectroscopic databases and our new data. A comparison with the atmospheric solar spectra measured using a ground-based Fourier spectrometer was carried. It was shown that the use of our new data on H_2O absorption line parameters improved the agreement the model and measured atmospheric spectra.

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Fourier transform spectrum of water vapor in the 9300 – 9800 cm^{-1} transparency window

T. Petrova[1], A. Solodov[2], O. Naumenko[3], V. Deichuli[3]

[1]V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev sq.,634055, Tomsk, Russia, [2] V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev sq., 634055, Tomsk, Russia, [3]V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences

A spectrum of natural water vapor is recorded in the 9300 – 9800 cm^{-1} transparency window using Bruker IFS 125HR high-resolution Fourier transform spectrometer (IAO, Tomsk). The records of the H_2O absorption spectra were made at temperature of 307K, the spectral resolution of 0.02 cm^{-1} with the optical path length of 105795 cm. The water vapor pressure was 0.0337 atm. About 720 weak water absorption lines between 9300 and 9800 cm^{-1} are assigned, about 300 of them are newly observed. Measured line intensities are compared both with available experimental data and calculated intensities included in the HITRAN2016 and GEISA2014 databases. Significant differences between the presently measured intensities and the corresponding data included in HITRAN2016 database were found for rotational- vibrational transitions of the (041) - (000) and (140) - (000) vibrational bands.

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ExoMol molecular line lists – XLIII: Rovibronic molecular line list for the two low-lying electronic states of NaO

G. Mitev[1], S. Taylor[1], J. Tennyson[1]*, S. Yurchenko [1], A. Buchachenko[3], A. V. Stolyarov[4]

[1] UCL Department of Physics and Astronomy , [2] UCL Department of Physics and Astronomy, [3]CEST, Skolkovo Institute of Science and Technology, [4]Department of Chemistry

Sodium oxide (NaO) is observed in airglows in the Earth's atmosphere and likely has astronomical importance. This study concerns the transitions with X $^2\Pi$ and to the very low-lying ($T_0 < 2000$ cm^{-1}) A $^2\Sigma^+$ state. A line list consisting of energy levels, allowed transitions, Einstein coefficients, and partition functions for varying temperature are produced based on variational solution of the coupled rovibronic Schrödinger equations using the program Duo as part of the ExoMol project [1]. Novel MRCI *ab initio* calculations characterising the potential energy curves, off-diagonal spin-orbit coupling curve, and (transition) dipole moment curves were integral in formation of final model. Furthermore, on-diagonal MRCI spin-orbit splitting for the X $^2\Pi$ state and the L-uncoupling matrix element curve between the X and A states are also calculated and presented. *Ab initio* PECs were parameterized into functional forms and refined by least-squares fitting to the available experimental data. Available assigned lines consisted of pure rotational transitions within the X $^2\Pi$ state for v = 0,1,2,3, $\Delta v = 0$ and electronic A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ transitions for v = 0, both with limited coverage over *J* (*J* up to 15.5, and up to 19.5 respectively) [2,3]. As there is a lack of data detailing the dissociation energies and vibrational structure of the X and A states, we are prompted to request further experimental study into the species which would allow further improvement of the model. The NaO line list is available via www.exomol.com.

The figure presented is the absolute absorption spectrum of the most recent NaO model at 400 K with comparison to the experimental spectrum from Joo et al [2].

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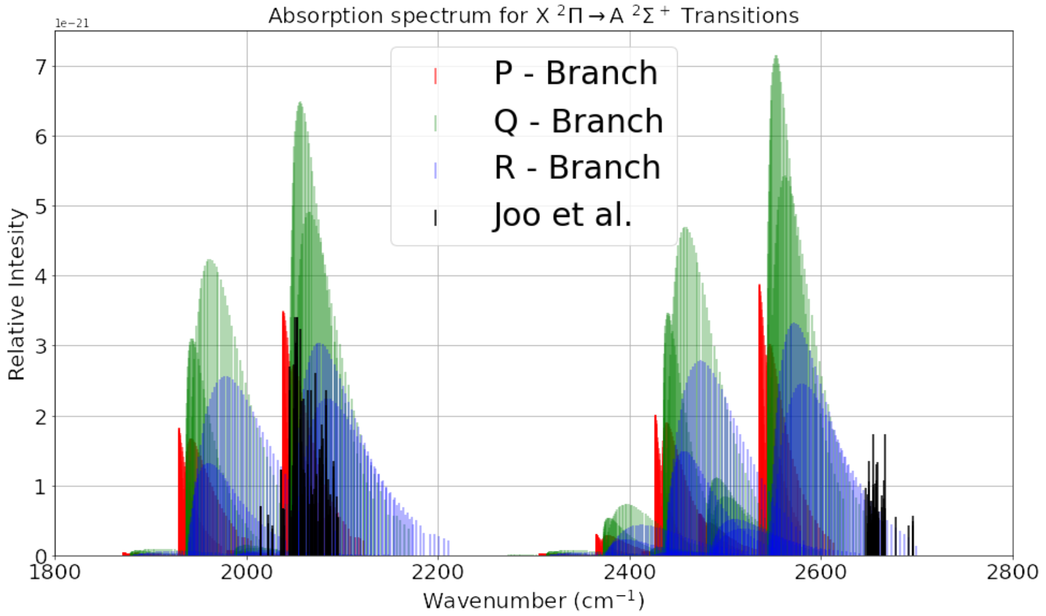

The Spectroscopic analysis of the v = 0 levels of the $B^2\Sigma^-$ and $D^2\Pi_i$ states of the CD radical

A. Para[1], W. Szajna[1], M. Zachwieja[1], R. Kępa[1], S. Ryzner[1], P. Kolek[1], I. Piotrowska[1], M. I. Malicka[1], R. Hakalla[1]*, J. Krełowski[1]*

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland

The stainless steel hollow-cathode lamp with two anodes and filled with a mixture of He buffer gas and CD_4 have been used in research. The emission from the discharge was observed with a high accuracy dispersive optical spectroscopy technique using a plane-grating spectrograph and recorded by a photomultiplier tube.

For the first time, the 0 - 1 band of the $B^2\Sigma^- - X^2\Pi$ system of the emission spectrum of the CD molecule was recorded and measured in laboratory conditions. Thanks to these results, our previous observations and analyzes [1] bands 0 - 0 of this system gained almost twice the number of molecular lines, significant in the analysis of the oscillation level v = 0. The result was a more perfect determination of the molecular constants of the vibrational level v = 0 of the $B^2\Sigma^-$ state, supplemented with the M_o centrifugal distortion constant. Based on the precise $B^2\Sigma^-$ state constants of the CD molecule and the wave numbers of the molecular lines [2] a new, more precise set of molecular constants of the $D^2\Pi_i$ state was obtained. The parameters of the Λ-doubling (p_o, q_o) and spin-rotation splitting (γ_o) of the $D^2\Pi_i$, of the v = 0 level were deduced for the first time. To reduce the experimental wavenumbers to rovibronic parameters the effective Hamiltonian involved in PGOPHER software was used [3].The present observations and analyzes have become the basis for a discussion on the possibility of detecting the CD radical in the interstellar medium. Initial lines of the $B^2\Sigma^- - X^2\Pi$, 0 - 0 band of CD were selected for astrophysical observation. This research is a continuation of the studies on the: $A^2\Delta - X^2\Pi$, $B^2\Sigma^- - X^2\Pi$ and $C^2\Sigma^+ - X^2\Pi$ systems in the CD radical made by our team [4-6].

Acknowledgments

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Theoretical and Microwave Spectroscopic Study of 5-Allyl-2-oxabicyclo[3.3.0]oct-8-ene and its Aggregates with Water

W. Sun[1], M. Schnell[1,2]*

[1] Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany, [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Kiel, Germany

5-Allyl-2-oxabicyclo[3.3.0]oct-8-ene (AOBO), as a chiral alkenyl ether, is widely used as a resolving reagent to protect/deprotect chiral alcohols in organic synthesis.[1] To better understand its conformational configurations, the pure rotational spectrum of AOBO in the gas phase was studied in the frequency range of 2-8 GHz using our COMPACT spectrometer. Four conformers arising from the orientation of the side-chain allyl group were assigned unambiguously with the assistance of quantum-chemical calculations performed at the B3LYP-D4/cc-pVQZ level of theory. Furthermore, the aggregation of water over the rigid cyclic system of AOBO through intermolecular hydrogen bonding was investigated. The aggregates with up to three water molecules have been identified in the spectrum. Interestingly, according to the spectral assignments, each of the four AOBO conformers was found to form at least one adduct with one water molecule in the supersonic jet. Additionally, the internal dynamics of the one-water complexes are explored.

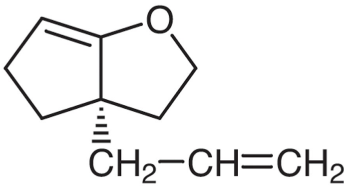

Fig. chemical structure of 5-allyl-2-oxabicyclo[3.3.0]oct-8-ene (AOBO).

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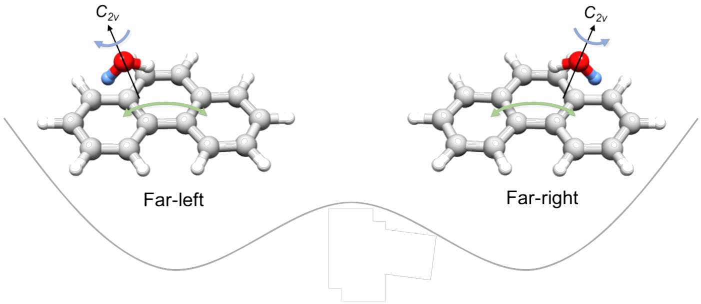
Concerted tunnelling motions in the phenanthrene-water cluster

D. Loru[1], A. L. Steber[1], C. Pérez[1,2], J. C. Lopez[2], B. Temelso[3], D. A. Obenchain[4], M. Schnell[1,5]*

[1]Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany, [2] Departamento de Química Física y Química Inorgánica, Facultad the Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain, [3]Division of Information Technology, College of Charleston, Charleston, SC 29424, USA, [4]Georg-August-Universität Göttingen, Institut für Physikalische Chemie, 37077 Göttingen, Germany, [5]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Straße 1, D-24118 Kiel, Germany

Gas-phase spectroscopic studies have shown that the water molecule can exhibit a high degree of internal dynamics both in complexes with itself and with other molecules. This, together with the nature of the interactions established with the substrate, influences the physical and chemical properties of many biological and chemical systems.

In this work, using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in combination with quantum-chemical calculations, we have investigated the internal dynamics in the phenanthrene-H_2O complex. In this system, the water molecule interacts with the substrate through weak O-H•••π hydrogen bonds, in which phenanthrene acts as the hydrogen bond acceptor via the high electron density of its aromatic cloud. The rotational spectrum exhibits interesting dynamical features which have been attributed to two concerted tunnelling motions: the water's internal rotation around the C_2 symmetry axis and the water's translation between the two equivalent peripheral rings of phenanthrene. The nature of these motions was further elucidated with the investigation of the splitting observed in the rotational spectra of the $H_2{}^{18}O$, D_2O and HDO isotopologues of the phenanthrene-H_2O complex. The barriers connecting the two equivalent isomers of the phenanthrene-H_2O complex and its isotopologues were determined using Meyer's flexible model.



High Resolution Rotation-Vibration Spectra of $^{M}SiD_4$ (M = 28, 29, 30) in the pentad region

A. V. Kuznetsov[1,2], O. V. Gromova[2], E. S. Bekhtereva[2], N. I. Raspopova[2], C. Leroy[1], K. Berezkin[3], C. Sydow[3], S. Bauerecker[3], O. N. Ulenikov[2]

[1]Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR CNRS 6303, Université Bourgogne Franche-Comté, Dijon Cedex 21078, France, [2]Research School of High–Energy Physics, National Research Tomsk Polytechnic University, Tomsk 634050, Russia, [3]Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D - 38106, Braunschweig, Germany

The first study of the absorption spectrum of the silane molecule in the pentad region was made. The high-resolution spectrum of the $^{28}SiD_4$ molecule in the range 1260-1480 cm^{-1} was recorded with a Bruker IFS 125HR Fourier transform interferometer and (0002, F_2), (0002, E), (0002, A_1), (0101, F_2), (0101, F_1), (0200, A_1) and (0200, E) vibrational states were theoretically analyzed. Rotational, centrifugal distortion, tetrahedral splitting, and resonance interaction parameters of the upper vibrational states were determined from the weighted least square fit method. Analogous analysis was made for the $^{29}SiD_4$ and $^{30}SiD_4$ isotopologues. The obtained set of parameters reproduces the initial ro-vibrational energy values of upper vibrational states with an accuracy of $d_{rms} = 3.6\times10^{-4}$ cm^{-1}.

Acknowledgments: The reported study was funded by the Russian Foundation of Basic Researches (RFBR), project number 20-32-90028.

Extended deperturbation treatment of the $A^1\Pi(v = 1)$ level in $^{13}C^{18}O$

S. Ryzner[1], M. I. Malicka[2], A. N. Heays[3], W. Ubachs[4], R. W. Field[5], N. de Oliveira[6], R. Hakalla[1]*

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland, [2]The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, Rzeszów, Poland, [3]J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic, [4]Department of Physics and Astronomy, and LaserLaB, Vrije Universiteit, Amsterdam, Netherlands, [5]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, USA, [6]Synchrotron SOLEIL, Orme de Merisiers, St. Aubin, France

The aim of this work was to reinvestigate the $A^1\Pi(v = 1)$ level in the $^{13}C^{18}O$ isotopologue. For this purpose, two complementary Fourier-transform techniques were used to obtain the spectra: *(i)* the emission spectroscopy in the visible region using Bruker IFS 125HR (University of Rzeszów) and *(ii)* the vacuum-ultraviolet absorption spectroscopy using the wave-front-division spectrometer working as the end station on the DESIRS beamline (SOLEIL synchrotron). In total, 588 wavenumbers of the B – A(0, 1), C – A(0, 1), A – X(1, 0), B – X(0, 0), C – X(0, 0), I – X(2, 0), and 6 interaction-induced bands were measured. A deperturbation analysis of the $A^1\Pi(v = 1)$ level in the $^{13}C^{18}O$ isotopologue was conducted on the basis of obtained data. In the analysis, an effective Hamiltonian and *the term-value fitting approach* were applied. As a result, 134 precise molecular parameters of the $^{13}C^{18}O$ investigated levels were obtained, including: molecular constants of the $A^1\Pi(v = 1)$, $I^1\Sigma^-(v = 2)$, $d^3\Delta(v = 6)$, $e^3\Sigma^-(v = 3)$ and $D^1\Delta(v = 1)$ levels; the rotation-electronic (***L***-uncoupling) $A^1\Pi(v = 1) \sim [D^1\Delta(v = 1), I^1\Sigma^-(v = 1), I^1\Sigma^-(v = 2)]$ and spin-orbit $A^1\Pi(v = 1) \sim [d^3\Delta(v = 6), e^3\Sigma^-(v = 3), a'^3\Sigma^+(v = 11)]$ interaction parameters; the spin-orbit/spin-electronic/***L***-uncoupling $a^3\Pi(v = 12) \sim d^3\Delta(v = 5)$ and spin-orbit $a^3\Pi(v = 12) \sim [D^1\Delta(v = 1), I^1\Sigma^-(v = 2)]$ perturbation parameters; as well as 112 ro-vibronic terms of $B^1\Sigma^+(v = 0)$ and $C^1\Sigma^+(v = 0)$ up to $J = 50$ and $J = 60$, respectively. The new results provide a significantly improved description of the $A^1\Pi(v = 1)$ and $a^3\Pi(v = 12)$ levels in $^{13}C^{18}O$ and their complex web of intra-molecular interactions compare to the previous one [1]. This research is a continuation of the studies on the $A^1\Pi$ state and its numerous perturbers in the CO isotopologues made by our team [2–5].

Acknowledgments

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New ab initio PES and DMS of $CClF_3$ and CCl_4 molecules

I. S. Chizhmakova[1,3], D. G. Malyshev[2,1], A. A. Rodina[2], A. V. Nikitin[2], M. Rey[3], V. G. Tyuterev[1,3]

[1]National Research Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia, [2]Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russia, [3]GSMA, UMR CNRS 7331, Université de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France

Chloro-trifluoromethane ($CClF_3$) and Carbon tetrachloride (CCl_4) molecules are among the ozone-depleting substances [1-2]. A modeling of infra-red spectra of these molecules can be helpful to better understand radiative properties of the Earth's atmosphere and to monitor the greenhouse gases. The calculation of ab initio spectra of such molecules is a part of the TheoReTS [3] project, for which the line lists of several greenhouse gases were previously produced [4, 5].

New potential energy surfaces (PES) of $CClF_3$ and CCl_4 molecules were constructed using extended *ab initio* CCSD(T) calculations at 22403 and 19882 nuclear configurations. The dipole moment surfaces (DMS) were also obtained in internal and in normal coordinates. The analytical representation of PES [6] and DMS [7] is determined by the decomposition into symmetry-adapted products of internal nonlinear coordinates with parameters up to the 6th and 4th orders respectively. Some lower vibrational energy levels were compared with observed data. Preliminary calculations of rotationally resolved spectra in the 600-3000 cm^{-1} range have shown a good agreement with PNNL [8] database.

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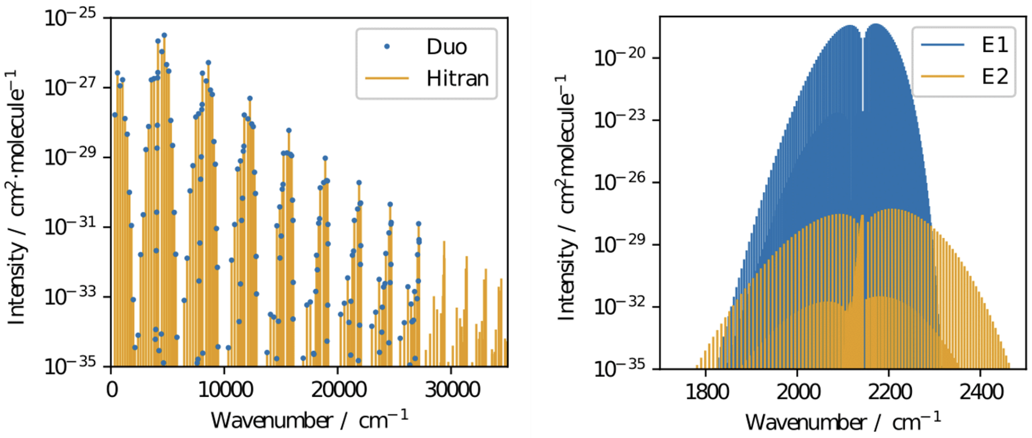
Calculations of the electric quadrupole moment function and transition linestrengths for diatomic molecules: Application to the X$^1\Sigma^+$states of H_2, CO and HF molecules.

W. Somogyi[1], S. Yurchenko[1]

[1]Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

The spectra of diatomic molecules are often treated using the electric dipole approximation. Owing to their molecular symmetry, many transitions of homonuclear diatomic molecules are forbidden by the electric dipole selection rules. Moreover, even when electric dipole transitions are present, for example in the spectra of heteronuclear diatomics, electric quadrupole transitions can still be observed and will contribute to molecular cross-sections. Accurate quadrupole line lists for the relevant species are crucial for reliable detection in exoplanetary atmospheres and many terrestrial applications. In this work we present a unified treatment of the electric quadrupole matrix elements, Einstein coefficients, and line strengths for general open and closed shell diatomic molecules in the general purpose Duo spectroscopic program. The implementation has been validated against accurate theoretical calculations and experimental measurements of quadrupole intensities of H2 available in the literature and against the electronic Noxon band in O2. We also present accurate electronic structure calculations of the electric quadrupole moment functions Θ(r) for the X3Σ+ states of CO and HF at the CCSD(T) and MRCI levels of theory, respectively. A demonstration of spectroscopic applications is provided by way of ab initio infrared electric quadrupole line lists for both molecules.



Left: Comparison of the Duo calculated absorption intensities with the intensities listed in the HITRAN database [1]
Right: The infrared rotational bands of the E1 and E2 rovibrational spectrum in the ground X$^1\Sigma^+$ state of the CO molecule. The E1 intensities are those of Li *et al.* [2]

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Rotational wave packet imaging spectroscopy of methane dimer $(CH_4)_2$: Effective structure and internal rotation

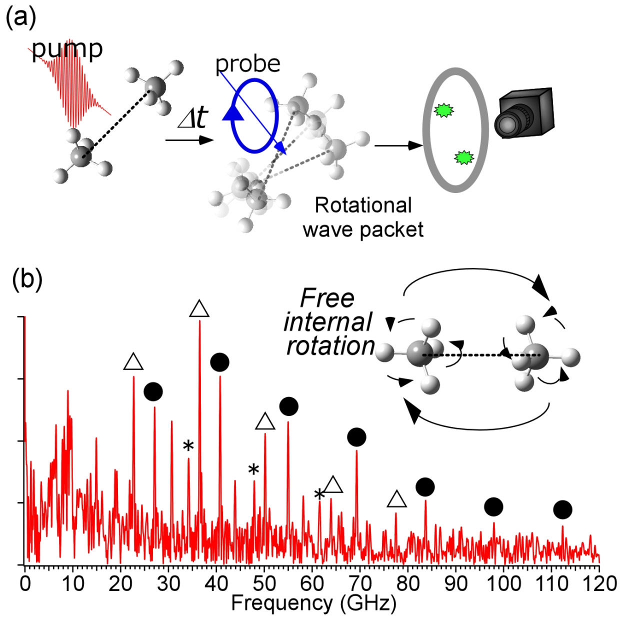
K. Mizuse[1,2], Y. Oyagi[2], Y. Tobata[2], Y. Ohshima[2]

[1]School of Science, Kitasato University, Japan, [2]Department of Chemistry, Tokyo Institute of Technology

Methane dimer is the smallest organic aggregate, of which structure and dynamics are governed by aliphatic-aliphatic intermolecular interaction. Despite its fundamental importance, high-resolution spectroscopy of methane dimer and clusters have been rare mainly because of their (almost) zero permanent dipole moment.

Recently, we have developed a method to record rotational Raman spectra of molecular dimers with very small dipoles. Our method relies onrotational wave packet imaging[1]. Rotational wave packet of a molecular dimer is created upon femtosecond pump, and subsequent dynamics is tracked by real-time Coulomb explosion imaging (Figure1 (a), [2]). Rotational Raman spectrum can be obtained as a Fourier transform of a time trace of an observed wave packet movie. Using such a wave packet imaging-based spectroscopy, we have measured rotational spectrum of $(N_2)_2$. Here, to extend our new method, and to study the nature of aliphatic-aliphatic intermolecular interaction, we have applied wave packet imaging spectroscopy to methane dimer.

Figure1(b) shows rotational Raman spectrum of $(CH_4)_2$ obtained as a FT of the observed time-trace of wave packet motion. The spectrum was analyzed on the basis of free internal rotor-based energy levels as in the case of $(N_2)_2$, CO-N_2, CH_4-Ne, and so on. In the observed spectrum we found at least three series with similar peak interval. From these series, we found that effective rotational constants of $(CH_4)_2$ are in the range of 3.4 to 3.65 GHz, corresponding to 400 to 420 pm of intermolecular distance. In high-level ab initio, the energy minimum lies in 368 pm. Such a contradiction suggests that the effective structures of $(CH_4)_2$ is governed by free internal rotation/zero-point vibration.



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Analysis of the CH_3D absorption spectrum in the 1.58 µm transparency window of methane

<u>A. Belova</u>[1], D. Mondelain[2], A. Campargue[2]*

[1]Tomsk Polytechnic Univ., 634050 Tomsk, [2]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble

The 1.58 µm methane transparency window, located between the tetradecad and icosad bands of CH_4, deserves to be characterized in details because it is important for planetary applications in particular for Titan and the giant planets. Unexpectedly, in spite of its low natural isotopic abundance (about 5×10^{-4}), CH_3D contributes greatly to the very weak absorption of methane in the region. In this work, the CH_3D absorption at room temperature and at 81 K are analyzed on the basis of (pure) CH_3D spectra recorded by high sensitivity differential absorption spectroscopy (α_{min} ~ 5×10^{-8} cm^{-1}). Some years ago, the corresponding line lists were constructed from these recordings for the 6200-6400 cm^{-1} region and empirical energy values, of the lower state level, E_{emp} were derived from the ratio of the intensities at 81 K and 294 K (the so-called 2*T*-method) [1]. In the present work, the line lists are extended to the 6100-6530 cm^{-1} range and includes 9000 and 8000 lines at 81 K and 294 K, respectively. About 4800 E_{emp} values are obtained using the 2*T*-method. In the considered region, previous rovibrational assignments were limited to about 400 transitions [2-4]. Our analysis of the 81 K spectra allowed for a significant extension of the assignments combining *(i)* the TheoReTs calculated line list [5,6] *(ii)* our set of derived E_{emp} values and *(iii)* ground state combination difference relations. Overall, more than 1300 lines could be assigned to the $3v_2$, $v_2+2v_5+v_6$ E, $v_2+v_4+v_6$ A_1, $3v_2$ A_1, $v_1+v_2+v_6$ E, and $v_2+v_4+v_6$ (E) bands.

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Conformational landscape and internal dynamics of limona ketone, a key oxidation product of limonene

N. Osseiran [1], A. Savoia [1], P. Dréan [1], T. R. Huet[1], M. Goubet[1]

[1]Université de Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, Lille 59000, France

Limonene, a biogenic volatile organic compound emitted by vegetation into the atmosphere, is one of the most abundant monoterpenes in atmosphere. Limonene and its oxidation product limonene oxide have been studied extensively in the last few years with rotational spectroscopy[1–3]. Limona ketone ($C_9H_{14}O$) is another oxidation product of limonene that is of atmospheric interest. It contains an acetyl functional group that can have equatorial and axial bonds.

The rotational spectrum of limona ketone was recorded in the gas phase using a Fourier transform microwave spectrometer coupled to a supersonic jet expansion over the 4 – 20 GHz range.[4,5] To display a complete view of the conformational landscape of this relatively flexible system, the relative stability and inter-conversion barriers between conformers were explored by electronic structure calculations. The lowest energy equatorial conformer was detected, and its spectroscopic molecular parameters were determined from the analysis of the spectrum. The internal rotation of the methyl group attached to the aldehyde moiety was taken into account in the analysis. Experimental lines of both A and E symmetry were fitted to experimental accuracy, and the experimental barrier height of the methyl group internal rotation is discussed with the support of quantum chemical calculations.[6]

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Line-shape parameters of H_2O perturbed by N_2 in the ~22000 cm^{-1} region

L. Sinitsa[1], V. Serdyukov[1], N. Lavrentieva[1], A. Dudaryonok[1], N. Lavrentiev[1], T. Nevzorova[2]*

[1]V.E. Zuev Institute of Atmospheric Optics, Siberia, [2]National Research Tomsk State University

The water vapor line contour parameters play an important role in the problems of atmospheric optics, remote sensing of greenhouse gases, and the environment. The water vapor line broadening and shifting coefficients for 36 strongest water vapor lines in the 22,330-22,590 cm^{-1} spectral region ($6\nu_1+\nu_3$ and $7\nu_1$ bands) induced by nitrogen pressure have been measured with a spectral resolution of 0.1 cm^{-1} at room temperature by a Fourier transform spectrometer using a high luminance LED source. The experimental spectra have been recorded by a FTS IFS-125M using a CREE XPE ARY high-brightness LED light source, which provides high sensitivity for recording the spectrum in the 0.45 µm region. A high signal-to-noise ratio ($S/N \approx 10\ 000$) allows one to analyze the lines with intensities from 1.25×10^{-25} to 1.15×10^{-26} cm/molecule. The calculations of the impact parameters of line contour have been performed by a semi-empirical method based on the semi-classical theory and using a correction factor for the efficiency function. The work used a water molecule energy levels and wave functions up to 30 000 cm^{-1}, the labeling of energy levels is based on the analysis of wave functions. A comparison with the available literature data, including in other absorption bands, is presented.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (V.E. Zuev Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Sciences). The experimental part of study was supported by the Russian Science Foundation (Grant No. 19-03-00389).

Light-emitting-diode Fourier transform spectroscopy of $H_2^{17}O$ in the range of 17000–19860 cm^{-1}

L. Sinitsa[1], A. Bykov[1], V. Serdyukov[1], E. Polovtseva[1], A. Scherbakov[1,1]

[1]V.E. Zuev Institute of Atmospheric Optics, Siberia

The high resolution absorption spectrum of $H_2^{17}O$ has been investigated between 17000 and 19860 cm^{-1} by Light-Emitting-Diode (LED) Fourier-Transform spectroscopy technique [1]. The spectrum has been recorded by IFS-125M Fourier spectrometer with spectral resolution of 0.1 cm^{-1}, at a pressure of 24 mbar, a temperature of 25°C, and an optical path length of 24 m. A multi-pass optical White's-type cell was used for measurements. A CREE XPE GRN bright LED was used as a source of radiation. The centers, intensities, and half-widths of lines were determined by fitting the Voigt profile convolved by the instrumental function to measured data by the least squares method. Triangular form of instrumental function was chosen for spectrum processing. The spectrum was identified using calculations of the EXOMOL group [2]. As a result of spectrum analysis, the centers and intensities of 159 lines have been determined for the first time. Additionally it has been obtained for the first time a set of 107 experimental energy levels belonging to the 5ν, 5ν+δ, and 6ν polyads of the resonant vibrational states. The obtained experimental data have been compared with calculated data [2]. The experimental data on the spectral line parameters and the energy levels found in this work [3] can be used to refine the available information on the water vapor absorption in the visible range.

This work was supported by RFBR (Grant No. 19-03-00389).

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New *ab initio* potential energy and dipole moment surfaces for non-rigid molecules: NH_3 and C_2H_6

O. Egorov[1,3], M. Rey[2], A. V. Nikitin[3,1], D. Viglaska[2]

[1]Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University 36, Lenin Ave., Tomsk, 634050 Russia, [2]Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France, [3]Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev Sq., Tomsk, 634055 Russia

New *ab initio* potential energy (PES) and dipole moment (DMS) surfaces for NH_3 are presented here. Along with the usual corrections due to one-electron relativistic and diagonal Born-Oppenheimer effects, our potential energy calculations include the electronic correlation contributions based on high order coupled-cluster algorithms. It turns out that the vibrational energy levels computed variationally from this pure *ab initio* PES (in the sense that no empirical corrections were applied) gives the lowest deviations from the experimental band centers tabulated in the MARVEL database [1], in comparison with other published pure *ab initio* NH_3 PESs [2–5]. This work also permitted to validate the newly developed model for nonrigid molecules [6,7]. Concerning C_2H_6, our previous work [8] was extended and a new *ab initio* DMS was built.

New algorithms were also developed for computing line intensities of nonrigid molecules in the frame of both curvilinear and normal mode coordinates. Finally, we will present a preliminary line list for NH_3 as well as the first vibrational energy levels for C_2H_6.

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LED based Fourier Transform Absorption Spectroscopy of $H_2{}^{17}O$ in 13300–14500 cm^{-1} Spectral Region

I. Vasilenko[1], O. Naumenko[1], V. Serdyukov[1], L. Sinitsa[1]

[1]V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Tomsk 634055, Russia

The vibration-rotation absorption spectrum of ^{17}O-enriched water vapor in the range 13320–14460 cm^{-1} was recorded by a Fourier Transform Spectrometer coupled to a multi-pass White-type cell providing an optical path length of 24 m at room temperature with a spectral resolution of 0.03 cm^{-1} using high luminance LED (light emitting diode) light source. The high signal-to-noise ratio allowed for the accurate determination of 1840 positions of water lines, of which 1080 lines were attributed to the $H_2{}^{17}O$ water isotopologue. The rovibrational assignment was based on new variational calculations [1] resulting in determination of 480 experimental rotational-vibrational energy levels belonging to eleven vibrational states of the $H_2{}^{17}O$ molecule: (301), (103), (221), (400), (023), (122), (202), (320), (141), (042), and (071). Previously, the Fourier absorption spectra of $H_2{}^{18}O$ and $H_2{}^{17}O$ in the range 11500 - 14500 cm^{-1} were studied in Ref. [2]. Of 480 energy levels presently determined, 270 levels are new. Transitions involving (320), (122), and (023) upper vibrational states at 13583.6, 13852.5, and 14015.5 cm^{-1}, respectively, are observed for the first time. A high quality of the new variational calculation [1] for $H_2{}^{17}O$ molecule is stated.

This work supported by RFBR (Grant was No. 19-03-00389)

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New ab initio potential energy and dipole moment surfaces of C_2H_2, $COCl_2$, and COH_2 molecules

A. A. Rodina[1,2], A. V. Nikitin[1], A. E. Protasevich[1], D. G. Malyshev[1,3], M. Rey[2], V. G. Tyuterev[3]

[1]V.E. Zuev Institute of Atmospheric Optics SB RAS, Akademician Zuev Sq 1., Tomsk, 634055 Russia, [2]Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France, [3]QUAMER laboratory, Tomsk State University 36, Lenin Ave., Tomsk, 634050 Russia

New potential energy surface (PES) of acetylene molecule was constructed using extended *ab initio* CCSD(T) calculations similar to one recently applied for the formaldehyde molecule [1]. We report theoretical rovibrational levels of acetylene computed from the PES and compare our results with other recent calculations [2]. New PES of $COCl_2$ describes qualitatively well all types of its vibrational motions. New DMS for all three molecules were constructed using ab initio CCSD(T) method. Preliminary calculations of rotationally resolved spectra of COH_2 and $COCl_2$ in the 600-3000 cm^{-1} range have shown a good agreement with experimental PNNL [3] absorption cross-sections. This study continues our TheoReTS project [4] devoted to the developing of complete theoretical line lists for polyatomic molecules relevant to atmospheric and astrophysical applications.

A.N. acknowledges support from RFBR grant number 19-03-00581.

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Simulation of rovibronic singlet-triplet transitions of $^{16}O_3$ near its first dissociation threshold

O. Egorov[1,3], R. R. Valiev[2,1], T. Kurten[2], V. G. Tyuterev[1,4]

[1]Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University 36, Lenin Ave., Tomsk, 634050 Russia, [2]Department of Chemistry, Faculty of Science, University of Helsinki, FIN-00014, Helsinki, Finland, [3]Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev Sq., Tomsk, 634055 Russia, [4]Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France

Due to new high-resolution measurements of the O_3 spectra in the region of its first dissociation threshold ($\approx$8560 cm^{-1}), the theoretical description of the observed rovibrational and rovibronic absorption patterns are currently of particular interest. We report the global calculation of the Franck-Condon factors for vertical electronic transitions between the ground singlet (X^1A_1) and $^3A_2$, $^3B_2$, and $^3B_1$ excited triplet states associated with the Wulf band of O_3. Our theoretical calculations were carried out at XMCQDPT2/aug-cc-pVQZ level of the theory including the static and dynamic electronic correlations. Along with the cold bands, a list of the strongest singlet-triplet hot bands falling into the region of the dissociation threshold of O_3 is presented. To obtain the intensities of the rovibronic transitions, the electronic transition dipole moments were computed. Finally, the rovibronic line intensities were calculated in absolute units for the most pronounced singlet-triplet hot bands located up to the first $^3A_2(000)\leftarrow X^1A_1(000)$ cold band inclusively. Comparisons with available experimental data are given.

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Isotopic relations for tetrahedral and octahedral molecules

M. Loëte[1], C. Richard[1], V. Boudon[1]

[1]Laboratoire Interdisciplinaire Carnot de Bourgogne

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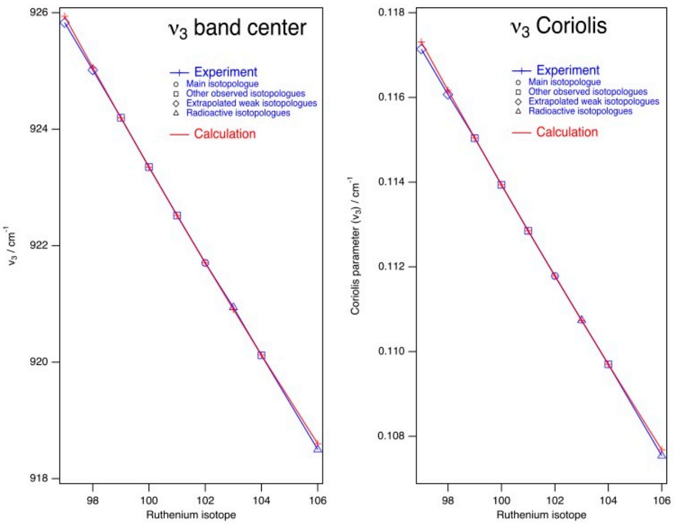
The study and analysis of heavy spherical-top molecules is often not straightforward. The presence of hot bands and of many isotopologues can lead to a high line congestion very difficult for assignment.

In this work, using a low-order model we have derived very simple iso- topic relations in order to determine initial parameters of the analysis [1]. We also show that an identical approach can be used for XY_4 and XY_6 molecules and all these results are illustrated by the comparison of numerical computations and experiments for different molecules: CH_4, GeH_4, RuO_4 (as shown in the figure) and SF_6.



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Millimeter-wavelength rotational spectra of carbon monoxide in argon bath in the pressure range from 0.01 up to 1500 Torr: analysis of the line shape and the continuum

E. A. Serov[1], T. A. Odintsova[1], A. A. Simonova[2], M. A. Koshelev[1], I. N. Vilkov[1], D. S. Makarov[1], A. A. Balashov[1,3], G. Y. Golubiatnikov[1], M. Y. Tretyakov[1]

[1]Institute of Applied Physics of the Russian Academy of Sciences, Nizhny Novgorod, Russia, [2]V.E. Zuev Institute of Atmospheric Optics, SB of the Russian Academy of Sciences, Tomsk, Russia, [3] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland

A study of molecular spectra in a broad pressure range is important for better understanding of the real spectrum shape, defined by intermolecular collisions. The total observed spectrum includes the contribution of individual resonant lines, whose shape depends on a number of different collisional effects (speed-dependent broadening and shifting, Dicke effect, line mixing, etc.), and smoothly varying with frequency non-resonant part or the continuum. The latter is supposed to appear as collision-induced absorption and absorption by molecular complexes. Studies of molecular spectra at near and above atmospheric pressures are relevant for radiative transfer modeling in dense atmospheres of planets. Radiation budget of such planets may strongly depend on quantitative characteristics of the continuum absorption caused by collisional interactions of atmospheric molecules.

Modern quantum-chemical methods allow to calculate *ab initio* molecular spectra with sub-percent uncertainty, although such calculations are possible only for a limited number of simple molecular systems [1,2]. The subject of the present study, CO-Ar system, is one of the respective examples. CO-Ar spectra were experimentally studied at room temperature in a broad pressure range using 3 spectrometers with complementary abilities: resonator spectrometer, spectrometer with radioacoustic detection (RAD) and video spectrometer. The first one allows investigating the broad lines and the continuum at pressures up to 2 atm. Its principle of measurement is similar to that of the cavity ring-down spectrometer, which makes it possible to determine the absolute absorption value. The RAD spectrometer operates at pressures ranging from 0.01 to 10 Torr. It is well suited for the line shape analysis in the line core region and measuring pressure broadening and shifting parameters of the lines and their speed-dependence. Our video spectrometer can be used in the pressure range from a fraction of mTorr to about 1 Torr. It allows accurate measurement of line frequency, intensity, pressure broadening and shifting parameters.

The manifestation of collisional effects in the rotational spectra of carbon monoxide mixed with argon was analyzed. Speed-dependent broadening and shifting coefficients, line mixing coefficients, and intensities of R(0) and R(1) lines were obtained from experimental data and compared with other theoretical and experimental results. The continuum absorption in pure CO and CO-Ar mixture was determined after subtraction the calculated contribution of the local lines. The determined continuum has the expected dependences on pressure and frequency. An analysis of these dependences allowed determining CO-CO and CO-Ar continuum coefficients for the first time.

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Molecular Line Lists for Hot Rocky Super-Earth Exoplanets

A. Owens[1], S. Yurchenko [1], J. Tennyson[1]

[1] UCL Department of Physics and Astronomy, Gower Street, London, UK

The atmospheres of hot rocky super-Earth exoplanets will have very different spectroscopic signatures compared to gas giants or cooler objects. Many of these exoplanets possess short orbital periods, hence hot atmospheres, and will have a lot in common with early Earth; the massive amounts of water and elevated temperatures are expected to turn the atmospheres into a (high pressure) steam bath containing the remains of melted rock.

We will present recent progress on the production of molecular line lists for hot rocky super-Earth exoplanets. A number of molecules containing silicon, alkali and alkaline earth metals are to be included in the ExoMol database. For the temperature and wavelength ranges considered, line lists will have to come from rigorous, first-principles calculations. However, these species pose new challenges and there is a pressing need for laboratory observations to improve the accuracy of our spectroscopic models.

First detections of electric-quadrupole transitions in water vapour

A. Campargue[1], S. Kassi[2], A. M. Solodov[3], A. A. Solodov[4], A. Yachmenev [5,7], S. Yurchenko[6]

[1]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, [2] Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France , [3]Laboratory of Molecular Spectroscopy, V.E. Zuev, [4]Laboratory of Atmospheric Absorption Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev sq., 634055, Tomsk, Russia, [5]Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany, [6]Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK, [7]Center for Ultrafast Imaging, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

Nowadays, the spectroscopic databases used for the modeling of the Earth and planetary atmospheres provide only electric-dipole transitions for polyatomic molecules (H_2O, CO_2, N_2O, CH_4, O_3…). Very recently, we have identified very weak electric-quadrupole (E2) transitions in the high sensitivity absorption spectrum of water vapor *(i)* near 1.3 µm by cavity ring down spectroscopy (CRDS) [A. Campargue et al. , Phys. Rev. Res., 2020, 2, 023091.DOI: 10.1103/PhysRevResearch.2.023091] and *(ii)* near 5.4 µm and 2.5 µm by Fourier transform spectroscopy (FTS) with kilometric absorption pathlength [A. Campargue, et al. PCCP, 2020, **22**, 12476 – 12481 10.1039/D0CP01667E]. These detections were performed on the basis of high accuracy *ab initio* predictions of the intensities of the E2 transitions. The experimental intensities are largely above the intensity cut-off of electric dipole transitions in standard spectroscopic databases and agree reasonably with the theoretical predictions. The calculated line list of E2 transitions, validated by the present measurements, has been incorporated in the HITRAN2020 line list of water vapor.

These first detections of E2 transitions in a polyatomic molecule paved the way to systematic searches of quadrupole transitions in other polyatomic molecules.

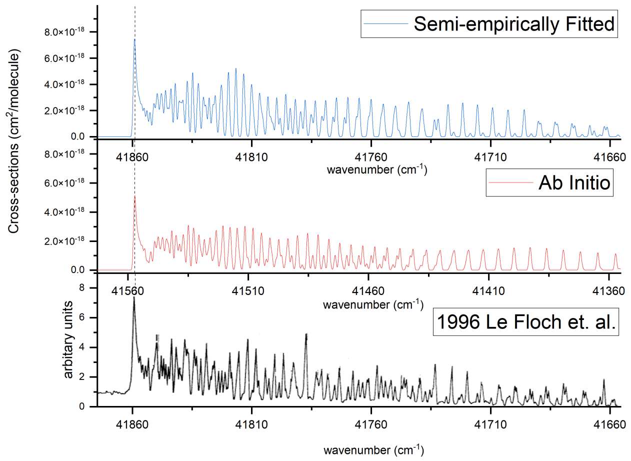
Ab Initio And Empirical Studies Of Electronically Excited States Of Phosphorus Mononitride (PN) And Its Rovibronic Spectroscopy

M. Semenov[1], N. El-Kork[2], S. N. Yurchenko [1], J. Tennyson[1]

[1] UCL Department of Physics and Astronomy ,Universi, [2]Physics Department, Khalifa University

We report an ab initio study on the rovibronic spectroscopy of the open-shell diatomic molecule phosphorous mononitride, PN. The study considers the nine lowest electronic states, $X^1\Sigma^+$, $A^1\Pi$, $C^1\Sigma^-$, $D^1\Delta$, $E^1\Sigma^-$, $a^3\Sigma^+$, $b^3\Pi$, $d^3\Delta$, and $e^3\Sigma^-$, using high-level electronic structure theory and accurate nuclear motion calculations. Using the ab initio data for bond lengths ranging from 1 to 3.16A, we compute 9 potential energy, 9 spin-orbit couplings, 7 electronic angular momentum coupling, 9 electric dipole moments, and 9 transition dipole moment curves.

The Duo [1] nuclear motion program is used to solve the coupled nuclear motion Schrodinger equations for these nine electronic states. The spectra of 31P 14N simulated for different temperatures are compared with several available high-resolution experimental studies. Lifetimes are calculated for all states and reported here with a comparison to previous results in the literature [2]. We then produce a separate line list for the $X^1\Sigma^+$, $A^1\Pi$, $E^1\Sigma^-$ states, with the potential energy functions and some couplings being fitted with the experimental energy values inverted using the MARVEL[3] procedure.



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Analysis of the accuracy of line intensities calculation using the Duo and Level programs

I. I. Mizus[1,3], L. Lodi[2,1], J. Tennyson[2], N. F. Zobov[1], O. L. Polyansky[2,1]

[1]Institute of Applied Physics, Russian Academy of Sciences, Ulyanov Street 46, Nizhny Novgorod 603950, Russia, [2] UCL Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK, [3]Holon Institute of Technology, Golomb Street 52, Holon 5810201, Israel

This work is dedicated to a problem of reaching an accuracy about 0.001 % while calculating of line intensities for rovibrational spectra of diatomic molecules, which is required for several applications including monitoring of the Earth's atmosphere, analysis of exoplanet atmospheres, and for some metrological purposes.

Here we present a careful analysis of a calculation accuracy for two program packages — the one named Duo and performed recently [1], and the older one, Level [2], each of which was designed for computing spectra and spectroscopic features of small diatomics. This analysis was performed on an example of three simplest cases: a quantum harmonic oscillator system, a fictitious Morse oscillator quantum system, and CO molecule considered as a quantum Morse oscillator. We call a system "fictitious" if it doesn't correspond to a real molecule and is considered just as one of the simplest quantum problems, which can be solved analytically.

The intensity of absorption line can be obtained using a matrix element value, thus the accuracy of matrix element calculations is of a high priority. We show that for the three systems listed above Duo supplies a similar or even a higher level of accuracy while obtaining of intensities and corresponding matrix elements than the one given by the Level package, and a satisfactory accuracy of calculations for stable state energies and corresponding wavefunctions. Moreover, Duo provides an accuracy level of CO diatomic matrix element calculations about 10^{-4}–10^{-5} % relative to the analytical values, which is sufficient for developing of accurate methods for experimental determination of some macroscopic gas features, like pressure, temperature, and so on.

The accuracy of the older package, Level, is particularly worse in the case of the fictitious harmonic oscillator-like system, when in calculations of matrix elements it shows the results, which are sometimes by two-three orders of magnitude worse than the corresponding Duo ones. Besides, to achieve a convergence in calculations using the Level package, we had to reduce grid step sizes by 10–20 times in comparison with the ones, which were used for the Duo calculations. As a direct consequence, there is a significant lack in productivity while calculating using Level in comparison with the Duo case. For instance, while computing of Einstein coefficients for CO molecule, Duo allowed to obtain the results by about 4.6 times faster then Level did using the same parameters except of the step size value when is was possible. Finally, the Duo package is much clearer in using.

We plan to continue this work by extending it to the case of polyatomic molecules and demonstrating the accuracy of the existing polyatomic codes, in particular DVR3D [3] for triatomic molecules and WAVR4 [4] for tetratomic molecules in the calculation of line intensities.

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New *ab initio* potential energy surface of the O_3–N_2 complex and calculation of its bound states

O. Egorov[1,3], Y. N. Kalugina[1], A. van der Avoird[2], V. G. Tyuterev[1,4]

[1]Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University 36, Lenin Ave., Tomsk, 634050 Russia, [2]Theoretical Chemistry, Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands, [3] Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev Sq., Tomsk, 634055 Russia, [4]Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France

Intermolecular interactions between O_3 and N_2 can play a key role in the formation reaction of stratospheric ozone, which is a multi-step collision process in the presence of a third body. Here we report a new five-dimensional *ab initio* potential energy surface (PES) of the O_3–N_2 van der Waals complex. *Ab initio* calculations were carried out for more than 90000 geometries of the complex using the explicitly-correlated single- and double-excitation coupled cluster method with a non-iterative perturbative treatment of triple excitations [CCSD(T)-F12a], and an augmented correlation-consistent triple zeta (aug-cc-pVTZ) basis set. The internal vibrational degrees of freedom of the monomers were frozen. The constructed PES shows a relatively deep global minimum (D_e= 348.88 cm^{-1}), with the N_2 monomer nearly perpendicular to the O_3 plane, as well as six local minima.

Bound rovibrational states were calculated for total angular momenta J = 0 and 1, with the use of the molecular symmetry group G_8. This yields the energy levels of O_3-orthoN_2 and O_3-paraN_2, but also the levels that are Pauli-forbidden for O_3 with ^{16}O. Rotational basis functions of the monomers were included up to j = 18 for O_3 and j = 11 for N_2 to converge the energy levels. The variational method applied is suitable for describing large amplitude internal motions in dimers, but we find for O_3–N_2 that these motions are rather restricted. The rovibrational wave functions were used to calculate dipole transition probabilities and to analyze the nature of the bound states.

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Global modelling of the observed line positions: Dunham coefficients for the ground $X^2\Pi$ state of ^{16}OH molecule

Y. G. Borkov[1], O. N. Sulakshina[1]

[1]V.E. Zuev Institute of Atmospheric Optics, SB RAS

A global treatment of all measured line positions for vibration-rotation, pure rotation transitions in the $X^2\Pi$ state and the measured line positions for vibrational bands of the $B^2\Sigma^+$-$X^2\Pi$ system, available in the literature for ^{16}OH molecule, was carried out. In the analysis, a global model with vibrational dependences of the parameters of the effective Hamiltonian for the diatomic molecule in $^2\Pi$ and $^2\Sigma$ electronic states was used. As a result of the fit, a set of the 'Dunham-type' molecular parameters was obtained. They reproduce the experimental dataset of the rovibrational and pure rotational transitions with experimental precision. The determined 'Dunham-type' molecular parameters were compared with those known previously.

Symmetries of CH_5^+

S. Brackertz[1], B. Nukic[1], P. Jensen[2], S. Schlemmer[1]*

[1]I. Physikalisches Institut, Universität zu Köln, [2]Faculty of Mathematics and Natural Sciences

Some time ago we developed a five dimensional SO(5) superrotor model [1] which describes the energy term diagram of the lowest energy states of CH_5^+ surprisingly well [2]. The basis for this model lies in the S 5 permutation symmetry of the five identical protons in this molecule. In this contribution we discuss possible sub-group structures, in particular the embedded $S_4 \otimes S_2 \subseteq S_5 \subset$ SO(5), which potentially simplifies the current model and more importantly can be associated with the internal motions (vibration/rotation/internal-rotation) of the molecule. As a result the ad-hoc SO(5) model motivated by the simple super-rotor energies can be replaced by a model justified by the underlying physics.

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Going to higher *J* values: new measurements and assignments in the $v_t = 0, 1$ torsional states of CD_3OH and CH_3OD

V. Ilyushin[1]

[1]Institute of Radio Astronomy of NASU, Mystetstv 4, 61002 Kharkiv, Ukraine

Co-authors: Y. Bakhmat[1], E. Alekseev[1,2], O. Dorovskaya[1], H. S. P. Müller[3], F. Lewen[3], S. Schlemmer[3], S. Bauerecker[4], C. Maul[4] , K. Berezkin[4,5], R.M. Lees[6], Li-Hong Xu[6]

[1]Institute of Radio Astronomy of NASU, Mystetstv 4, 61002 Kharkiv, Ukraine; [2]Quantum Radiophysics Department, V.N.Karazin Kharkiv National University, Kharkiv, Ukraine; [3]I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany; [4]Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Gaußstr. 17, 38106 Braunschweig, Germany; [5]National Research Tomsk Polytechnic University, Tomsk 634050, Russia; [6]Department of Physics, University of New Brunswick, Saint John, NB E2L 4L5, Canada.

We present[a] the results of our new study of the torsion-rotation spectra of two deuterated isotopologues of methanol: CD_3OH and CH_3OD. The new microwave measurements were carried out using spectrometers in Kharkiv and Köln (in total from 34 GHz up to 1.1 THz). For CD_3OH microwave measurements were augmented by new FIR measurements in the range 20 to 900 cm^{-1} carried out in Braunschweig. In this work we significantly extend the rotational quantum number coverage for both isotopologues (from $J_{up} = 26$ [1] to $J_{up} = 55$ for CD_3OH and from $J_{up} = 21$ [2] to $J_{up} = 44$ for CH_3OD). The analysis is done using the rho axis method and the RAM36 program code. For both isotopologues the $v_t = 2$ torsional state is significantly affected by intervibrational interactions with non-torsional vibrational modes which propagate down through intertorsional interactions. Thus we decided to concentrate our efforts on analysis of the $v_t = 0, 1$ states at the moment. For CD_3OH we were able to get a fit within experimental error for the $v_t = 0, 1$ states. For CH_3OD the analysis is in progress. In the talk the details of this new study will be discussed.

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The Shapes of Sulfonamides: The Rotational Spectra of Benzenesulfonamides, *ortho*-Toluensulfonamide, *para*-Toluensulfonamide and Sulfanilamide

S. Melandri[1], A. Maris[1], M. Sanz[2], D. Loru[2], I. Pena[2], C. Calabrese[1]

[1]University of Bologna, Department of Chemistry , [2]King's College London, Department of Chemistry

The effects of substitution were investigated for the sulfonamides class of molecules, in particular those which contain the benzosulfonamide functional group. This group of molecules is of extreme interest in the biological field since many of them are active against a variety of diseases. In this work, structural investigations on the pharmacophoric group benzensulfonamide and the substitution effects have been performed through the studies of its derivatives benzensulfonamide itself, *para*-toluensulfonamide, *ortho*-toluensulfonamide and the bioactive molecule sulfanilamide. In all compounds, but in *ortho*-toluensulfonamide, the amino group lies perpendicular to the benzene plane with the amminic hydrogens eclipsing the oxygen atoms. In *ortho* -toluensulfonamide where a weak attractive interaction between the nitrogen lone pair and the methyl hydrogen atoms takes place, the amino group lies in the *gauche* orientation. These results show that such weak non-covalent interactions are able to change the conformational preferences of the pharmacophoric group.

For all species, the ^{14}N quadrupolar hyperfine analysis has been performed. This has provided crucial information for the unambiguous identification of the observed conformation and the structural parameters related to the position of the nitrogen atom. In addition, for *ortho* -toluensulfonamide, the vibration-rotation hyperfine structure related to the methyl torsion has been analyzed and the methyl group rotation barrier was determined.

Microwave Spectroscopic and Quantum Chemical Investigations on 2,4-Dimethylpyrrole

L. Nguyen[1], M. Barth[2]

[1]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), [2]Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany

The effects of methyl internal rotation in aromatic compounds is not a simple issue due to electrostatic interactions expanded through the conjugated p-system. If a ^{14}N nucleus is present in addition, quadrupole hyperfine structures occur in the microwave spectrum, giving us information on the electric field gradient at the site of the ^{14}N nucleus and consequently on the nature of its chemical bonds, but on the other hand also increasing the complication of the spectral features. In 2,4-dimethylpyrrole (24DMP), torsional fine splittings arising from two inequivalent methyl groups interfere with the ^{14}N hyperfine splittings, which were both investigated using a combination of quantum chemical calculation and microwave spectroscopy.

The microwave spectrum of 24DMP was recorded using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2 to 26.5 GHz [1]. The complicated fine and hyperfine structures were successfully assigned and fitted using the program XIAM. The torsional barriers were determined to be about 254 cm^{-1} and 284 cm^{-1} for the methyl rotors at the second and the fourth ring position, respectively. The ^{14}N quadrupole coupling constants could be accurately determined.

Finally, the torsional barrier of the methyl rotor adjoining the nitrogen atom can be compared to that found for 2,5-dimethylpyrrole [3] and 2-methylpyrrole [4] and that of the methyl group at the fourth ring position with that of 3-methylpyrrole [5]. Due to the Cs symmetry of all molecules, the values of ccc could be directly compared with each other and with that of other aromatic five-membered rings. Different signs of the ccc constant can be explained by the different chemical bond situations.

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Near-infrared Vibronic Spectrum of the First Excited State of Au_2^+

O. Dopfer[2], K. Pollow[2], T. Studemund[2], M. Förstel[2]*

[1]Institut für Optik und Atomare Physik (TU Berlin, Germany), [2]Institut für Optik und Atomare Physik (TU Berlin,

The often unusual chemical properties of small gold clusters arise from several factors, including strong spin-orbit coupling, contributions of *d*-orbitals to chemical bonding, and large relativistic effects. The typical multi-reference character of their excited electronic states, which are relevant for catalytic processes, provide high challenge for quantum chemical calculations, which are required to understand electronic structure and chemical reactivity at the molecular level. High-resolution experimental spectra provide useful benchmarks for developing and testing such quantum chemical approaches. Recent progress in instrumentation with respect to sensitivity and resolution (by two orders of magnitude) has allowed our group to record for the first time vibrationally-resolved electronic spectra of small and cold Au_n^+ cluster cations, such as Au_4^+ and Au_2^+, by means of photodissociation spectroscopy in a temperature-controlled laser desorption source coupled to a quadrupole/time-of-flight tandem mass spectrometer and a broadly tuneable midband OPO laser system [1,2,3]. Such spectra are still extremely scarce for transition metal cluster cations. Au_2^+ is a simple but crucial model system for understanding the diverse catalytic activity of gold. While the Au_2^+ ground state ($X^2\Sigma_g^+$) is understood reasonably well from mass spectrometry and computations, no spectroscopic information is available for its first excited state ($A^2\Sigma_u^+$). Herein, we present the vibrationally-resolved electronic spectrum of the first excited state of cryogenic Ar-tagged Au_2^+. The exceptionally low-lying and well-isolated $A^2\Sigma_{(u)}^+ \leftarrow X^2\Sigma_{(g)}^+$ transition occurs in the near-infrared (NIR) range and shows a regular vibrational pattern of a linear triatomic molecule. The observed band origin (5738 cm^{-1}, 1742.9 nm, 0.711 eV) and harmonic Au-Au and Au-Ar stretch frequencies (201 and 133 cm^{-1}) agree surprisingly well with those predicted by standard time-dependent density functional theory calculations. The linearly-bonded Ar tag has only little impact on the geometric and electronic structure of Au_2^+, because the Au_2^+...Ar bond (0.4 eV) is much weaker than the Au-Au bond (2.2 eV). As a result of 6s←5d excitation of an electron from the antibonding σ_u^* orbital (HOMO-1) into the bonding $_{\sigma g}$ orbital (SOMO), the Au-Au bond contracts substantially (by 0.1 Å). In contrast to the A state, higher lying electronic states of Au_2^+ show a very irregular pattern due to strong vibronic coulping between multiple close-lying electronic states [3].

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New level of accuracy in variational calculations of bound and metastable states and of line intensities of the ozone molecule

V. G. Tyuterev[1,3], V. Kokoouline[2], A. Alijah[3], S. Tashkun[2], R. V. Kochanov[1,3], O. Egorov[1,3]

[1]Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University 36, Lenin Ave., Tomsk, 634050 Russia, [2]Department of Physics, University of Central Florida, Orlando, FL 32816, USA, [3]Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France

Recent results on the theory of the ozone spectral patterns in the infrared will be presented. This includes ab initio calculations providing a sub-percent accuracy for line intensities of vibration-rotation bands in the strongly absorbing regions [1,2] as well as significant improvements for the bands origins of the isotopic species [3,4]. The implications of Jahn-Teller effect producing the delocalization of highly excited states in the three potential wells [5], which have been recently confirmed by laser spectra measurements and analyses [6] will be discussed. Metastable levels above the dissociation threshold and their lifetimes for the ^{18}O-enriched isotopomers are computed using accurate ab initio the potential energy surfaces with two versions of the shape in the transition state range, and the impact on the dynamics of isotopic exchange reactions [7] will be overviewed. The work was supported by RNF project No. 19-12-00171.

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Microwave spectrum of the first excited torsional states of dimethylether $(CH_3)_2O$.

V. Ilyushin[1,5], Y. Bakhmat[1], E. Alekseev[1,5], O. Dorovskaya[1], B. Drouin[2], S. Schlemmer[3], H. S. Müller[3], C. Endres[4]

[1]Institute of Radio Astronomy of NASU, Mystetstv 4, 61002 Kharkiv, Ukraine, [2]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, USA, [3]I. Physikalisches Institut, Universität zu Köln, [4]Max Planck Institute for extraterrestrial Physics, Giessenbachstrasse 1, 85748 Garching Bayern Germany, [5]Quantum Radiophysics Department, V.N.Karazin Kharkiv National University, Kharkiv, Ukraine

Microwave transitions belonging to the three lowest torsional states of dimethylether (DME), $(CH_3)_2O$, have been analyzed using the recently developed model for molecules with two equivalent methyl rotors and C_{2v} symmetry at equilibrium (PAM_C2v_2tops program) [1]. The dataset comprises not only assignments from the literature and previous measurement campaigns (ground state [2], torsional excited states [3,4]), but also new measurements. These new measurements have been carried out using the Kharkiv spectrometer in the Institute of Radio Astronomy of NASU (Ukraine) from 49 GHz to 180 GHz and from 255 GHz to 400 GHz. Significant progress in fitting transitions within the first excited torsional states corresponding to the two methyl torsional modes in DME has been achieved and the comprehensive dataset has been reproduced within experimental accuracy by our fit. New assignments contain not only the pure rotational transitions within the studied torsional states but also about 500 intertorsional transitions connecting the two torsionally excited states which are observable in the microwave range due to intensity borrowing. Details of the experimental dataset, its analysis and the fit as well as the problems we encountered will be discussed.[a]

[a]This work was done under support of the Volkswagen foundation. The assistance of Science and Technology Center in Ukraine is acknowledged (STCU partner project #P686a).

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Molecular recognition in olfaction: interactions of the odorant carvone with ethanol

S. I. Murugachandran[1], D. Loru[2], I. Pena[2], M. Sanz[2]*

[1]King's College London , [2]Department of Chemistry

Non-covalent interactions are vitally important for molecular recognition in many biological and chemical processes. Understanding the interplay between intra- and intermolecular forces is crucial for advancing our knowledge on these events and how they are influenced by slight changes. Here we report the interactions of the common odorant carvone with ethanol, a mimic to the amino acid side chain serine. It has been studied through combination of chirped-pulse Fourier transform microwave spectroscopy and computational calculations, including density functional theory and *ab initio* methods. Two carvone-ethanol complexes have been observed showing an O····H-O primary bond between the carbonyl group of carvone, acting as a hydrogen bond acceptor, and the hydroxyl group of ethanol as the hydrogen bond donor. Secondary C-H····O dispersion interactions anchoring ethanol to carvone are also established.

Hyperfine effects in the vibrational spectroscopy on the $Cl^-(H_2)$ complex

F. Dahlmann[1], C. Lochmann[1], A. Marimuthu[2], M. Lara-Moreno[3], R. Wild[1], S. Schlemmer[4], P. Halvick[3], T. Stoecklin[3], O. Dulieu[5], S. Brünken[2]*, R. Wester[1]*

[1]University of Innsbruck, [2]Radboud University, [3]Université de Bordeaux, [4]I. Physikalisches Institut, Universität zu Köln, [5]University Paris-Saclay

Predissociation spectra of the $^{35}Cl^-(H_2)$ complex are measured at low frequencies between 400 and 800 cm^{-1} in a 22-pole ion trap instrument at the FELIX Laboratory [1] at different temperatures. While the linear complex of Cl^-(*para*-H_2) is nearly indistinguishable from Cl^-(*ortho*-H_2) in their respective ground states, in the dissociation limit they correlate to different rotational states, with a significant energy gap of about 200 cm^{-1}. Thus, in their excited vibrational states the different spin isomers show very different eigenstates and as a result, differ substantially in their vibrational spectra.

At low temperatures, we observe a complete conversion of the Cl^-(*para*-H_2) to the Cl^-(*ortho*-H_2) complex, which is the more strongly bound complex. This switching is driven by the interaction between Cl^- and *para*-H_2, which is weaker than the interaction with *ortho*-H_2 due to the absence of a quadrupole moment, and the approx. 110 cm^{-1} higher binding energy of the *ortho*-H_2 complex [2]

Cl^-(*para*-H_2) + (*ortho*-H_2) → Cl^-(*ortho*-H_2) + (*para*-H_2) + ΔE

As a result, only the Cl^-(*ortho*-H_2) complex can be detected at 14 K. [4] Performing the experiment at high enough temperatures the reaction can proceed in both directions and both hyperfine complexes remain present. Above approx. 30 K, we could therefore detect the two most intense para bands with their maxima at 510(1) and 606(1) cm^{-1}.

The experimental spectra are compared with calculations, computed by an accurate quantum approach. [3] The two main bands have been assigned to the rovibrational resonant states $2\nu_2$ and $\nu_1 + 2\nu_2$, a progression of the intermonomer vibrational stretching mode between the Chlorine anion and H_2. Due to the large mass difference, unique for this kind of complexes, the tunneling splitting plays an important role here. The calculated spectra are shifted to the red by about 9 cm^{-1}. This discrepancy might be attributed to accuracy of the employed potential energy surface. The *para* to *ortho* ratio is compared to the expectation based on the forward and backward ligand switching reactions.

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Highly accurate HF dimer *ab initio* potential energy surface

R. I. Ovsyannikov [1], V. Y. Makhnev[1], N. F. Zobov[1], J. Koput[2], J. Tennyson[3], O. L. Polyansky[1,3]

[1]Institute of Applied Physics Russian Academy of Sciences, Ulyanov Street 46, Nizhny Novgorod, Russia 603950, [2]Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland, [3]University College London, Gower Street, London, WC1E 6BT, United Kingdom

In this work, a very accurate, $(HF)_2$ potential energy surface (PES) is constructed based on ab initio calculations performed using the MOLPRO package at the CCSD(T)-F12b level of theory with an aug-cc-pvQz-F12 basis set at about 161000 points. A higher correlation correction is computed at CCSDT(Q) level for 2000 points and is considered alongside other more minor corrections due to relativity, core-valence correlation and Born-Oppenheimer failure.

Calculations over an extended range of rotationally excited states show very good agreement with the experimental data. In particular, the known empirical rotational constants B [1] for the ground vibrational states are predicted to better than about 2 MHz. B constants for excited vibrational states are reproduced several times more accurately than by previous calculations [2]. This level of accuracy is shown to extend to higher excited inter-molecular vibrational states ν and higher excited rotational quantum numbers (J, Ka).

The study of weakly bound molecular complexes with hydrogen bonds and Van der Waals bonding accounts for a large sub-branch of molecular spectroscopy. Intermolecular states with (J, K>1) of the most interesting one -- $(H_2O)_2$ -- currently cannot be characterized in high resolution experiments [3]. As a consequence of the considerable similarity of this system to $(HF)_2$ system, the HF dimer discrepancies provide a unique means of characterizing the corresponding discrepancies in water dimer spectra. Hence, a high level ab initio model for the rotation-vibration-inversion (RVI) spectrum of the HF dimer will be an important aid in constructing a similarly accurate mode for the RVI spectrum of the water dimer.

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Accurate IR spectra of formyl cation (HCO^+) derived from new potential energy and dipole moment surfaces.

V. Y. Makhnev[1], A. A. Kyuberis[2], N. F. Zobov[1], J. Tennyson[3], O. L. Polyansky[1,3]

[1]Institute of Applied Physics Russian Academy of Sciences, Ulyanov Street 46, Nizhny Novgorod, Russia 603950, [2]Van Swinderen Institute for Particle Physics and Gravity, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands, [3]University College London, Gower Street, London, WC1E 6BT, United Kingdom

The formyl cation is an important ion in astrophysical studies. As the second (after CH^+) and the first triatomic ion to be detected in interstellar space [1], HCO^+ takes an important part of processes in many space objects. As a significant example, recent work by Bourgalais *et al.* [2] raises the possibility that HCO^+ is relatively abundant in the atmospheres of exoplanets where CO and N_2 are present.

In this work we present a new spectroscopic model for HCO^+: a) a new potential energy surface (PES) for the electronic ground state constructed by refining our unpublished *ab initio* PES to existing experimental data (this PES gives very similar discrepancies to the ab initio PES by Koput [3]); b) a new *ab initio* dipole moment surface (DMS) based on MRCI calculations.

Our experience in variational calculations shows the need for excellent wavefunctions along with high-level dipole calculations for intensity calculations. For this purpose we adjusted *ab initio* PES based on ~700 aug-cc-pCV6Z energies up to 25000 cm^{-1} by the set of experimentally-derived data from Nesse *et al.* [4]. This optimized PES allows to reproduce rovirational energy states with accuracy better than 0.1 cm^{-1}.

A new *ab initio* high accuracy dipole moment surface of HCO^+ is constructed. The IC-MRCI all-electrons method was used for dipole moment calculations, dipole points in ~700 configurations were computed using external field method and reproduced by polynomial functional form with less than 10^{-5} Debye standard deviation.

The new empirical PES and *ab initio* DMS are used to calculate spectra of formyl cation at IR wavelengths. Because of the lack of experimental data for this molecule we can predict at best the accuracy of intensities within 2% for the strongest bands and

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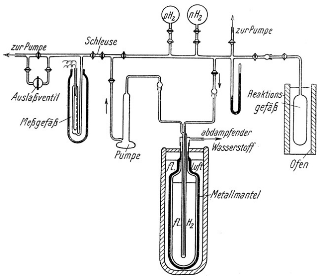
Para-ortho hydrogen conversion; solving a 90-year old mystery

A. van der Avoird[1], X. Zhang[1,3], T. Karman[2,1], G. C. Groenenboom[1]

[1]Theoretical Chemistry, Radboud University, Nijmegen (NL), [2]Center For Astrophysics, Harvard & Smithsonian, Cambridge MA, USA, [3]Institute of Atomic and Molecular Physics, Jilin University, Changchun, China

It is well known among spectroscopists that hydrogen has two modifications: para-H_2 and ortho-H_2. Pure para-H_2 can be produced by leading “normal” H_2, a 3:1 ortho:para mixture, over a catalyst at low temperature. It is perhaps less well known that para-ortho H_2 conversion is also catalyzed by collisions with paramagnetic molecules, such as O_2.



Almost ninety years ago Farkas and Sachsse [1] measured the rate coefficient of para-ortho H_2 conversion in gas mixtures with O_2, with the setup shown in the figure. In the same year, 1933, it was proposed by Wigner [2] that it is the magnetic dipole-dipole coupling between the electron spin of O_2 and the spins of the two protons in H_2 that is responsible for the conversion. In asymmetric collisions this coupling makes the two H-nuclei inequivalent and mixes the nuclear spin functions of para- and ortho-H_2, as well as their rotational states with even and odd *j* values. Another mechanism, suggested to be much more effective, was proposed later: the exchange interaction with the open-shell O_2 induces spin density into the electronic wavefunction of H_2. In most collisions the spin density is different at the two H-nuclei, which makes them inequivalent by different hyperfine interactions through the Fermi contact term.

An important application of para-H_2 is in NMR spectroscopy and its imaging variant, MRI. By adding para-H_2 to the sample the sensitivity of NMR can be increased by four orders of magnitude by a phenomenon called para-hydrogen induced polarization (PHIP). Para-ortho H_2 conversion by O_2 in the gas phase was remeasured [3] in 2014 in view of this application. A detailed and quantitative understanding of the conversion process was still lacking, however.

We theoretically investigated [4] para-ortho H_2 conversion by collisions with O_2 in a first principles approach. Both mechanisms were taken into account and the corresponding coupling terms were quantitatively evaluated as functions of the geometry of the O_2-H_2 collision complex by means of ab initio electronic structure calculations. Then they were included in nearly exact quantum mechanical coupled-channels scattering calculations for the collisions between O_2 and H_2, which yielded the para-ortho H_2 conversion cross sections and the rate coefficients for temperatures up to 400 K. The conversion rate and its temperature dependence are in good agreement with the values measured in H_2-O_2 gas mixtures. The calculations provide detailed insight into the conversion process.

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Recent developments and future challenges in molecular quantum theory

E. Mátyus[1]

[1]ELTE, Eötvös Loránd University, 1117 Budapest, Pázmány Péter sétány 1/A

High and ultra-high precision spectroscopy experiments of small molecular systems make it possible to test and further develop the fundamental theory of molecular matter. The molecular and atomic range of matter is governed by quantum mechanics and the constituent particles, the electrons and the atomic nuclei, interact by electromagnetic interactions. Although the Lagrangian density of relativistic quantum electrodynamics is standard textbook material, it is a non-trivial task to write down the most possible complete wave equation (that fulfills basic requirements, like Lorentz invariance) and that could be solved (numerically) to high precision [1,2]. To compute bound and quasi-bound molecular states [3,4,5], series approximations have been traditionally evoked in terms of the small parameters of the theory: the $(m_\mathrm{e}/m_\mathrm{p})^{1/2}$ square root of the electron-to-proton mass ratio [6], the α fine-structure constant and the $Z\alpha$ nuclear-charge-number multiple of the fine structure constant [7]. The series expansions of the relativistic QED description of few-body systems lead to the fundamental concepts currently in use, *e.g.,* the Schrödinger equation and the Born‒Oppenheimer approximation to describe the structure and dynamics of molecular systems [8,9]. Furthermore, the series expansions result in a number of "effects" that needs to be accounted for by perturbation theory, if a quantitative theory-experiment agreement is sought for. Comparison with experiments of high energy resolution [10] shows that the "small" effects often ignored (or approximated) are "visible" and important, their partial cancellation cannot be predicted *a priori,* moreover, the relative magnitude of the corrections changes from system to system and from transition to transition [11]. Although the perturbative non-adiabatic and relativistic approaches support our current intuitive picture of molecular processes at low orders, the higher-order corrections, necessary for a quantitative agreement with the most precise experiments, become increasingly complicated (formally and numerically) and are always limited to some finite order. For this reason, I will speak about complementary, perturbative [6,12] and variational [1‒5] approaches to the non-adiabatic and relativistic problems of molecular quantum theory. I will sketch theoretical, algorithmic, and computational challenges that were recently met and that are still open for small atomic and molecular systems in relation with (ultra-)high-resolution spectroscopy experiments.

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Parallel Session: Internal rotation, Contributed Talk (15min) **CA1**

Internal rotation in a loosely bound ion-rare-gas complex: He-H_3^+

T. C. Salomon[1], O. Asvany[1], D. Gerlich[2], I. Savic[3], A. van der Avoird[4], M. E. Harding[5], F. Lipparini[6], J. Gauss[7], S. Schlemmer[1]*

[1]I. Physikalisches Institut, Universität zu Köln, Köln, Germany, [2]Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany, [3]Department of Physics, University of Novi Sad, Novi Sad, Serbia, [4]Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands, [5]Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany, [6]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy, [7]Institut für Physikalische Chemie, Universität Mainz, Mainz, Germany

The ro-vibrational predissociation spectrum of He-H_3^+ has been recorded via excitation of the □ν_2 vibrational mode of the H_3^+ sub-unit in the 22-pole ion trap experiment COLTRAP. The spectrum for the bare H_3^+ consists of only a few ro-vibrational lines each for the para and ortho nuclear spin configuration, respectively. Instead, the spectrum of the complex is very rich (severalhundred lines) even at the low experimental temperatures (4 K). Part of this complexity is associated with the (almost) free internal rotation of H_3^+. The experimental results are compared to theoretical predictions of ro-vibrational spectra on the basis of ab-initio calculations of the H_3^+ potential energy surface. The energy levels result in transitions which agree in many cases with experimental results within a few wavenumbers. In particular the typical band structures of a P- and R-branch associated with an effective diatomic complex seen in the experimental and predicted spectrum help in assigning the rich spectrum. Moreover, an experimental energy term diagram is reconstructed from the observed transitions which can be compared to the rather accurate theoretical predictions. The system is discussed using the approach of Jeremy M. Hutson [1] typically used to describe the dynamics of Van der Waals molecules. The influence of the Coriolis interaction in a case 2 coupled complex resulting from the H^+_3 internal rotation in a rotating He-H^+_3 is discussed.

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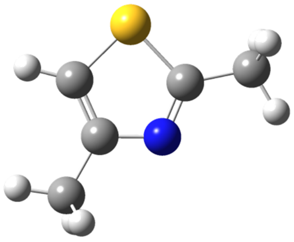
Methyl internal rotations and ^{14}N quadrupole coupling in the microwave spectra of 2,4-dimethylthiazole and 4-methyl-5-vinylthiazole

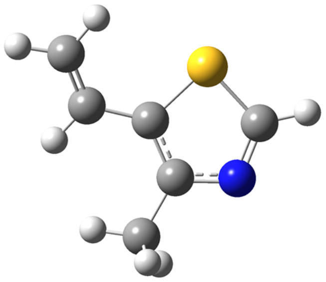
S. Khemissi[1], I. Kleiner[1], M. Schwell[1], L. Nguyen[1,2]

[1]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7583, Université Paris-Est Créteil, Université de Paris, 61 avenue du Général de Gaulle, F-94010 Créteil, France, [2] Institut Universitaire de France (IUF), 1 rue Descartes, 75231 Paris cedex 05, France

The rotational spectrum of two thiazole derivatives, 2,4-dimethylthiazole (24DMTA) and 4-methyl-5-vinythiazole (MVT), were measured using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2.0 to 26.5 GHz. In MVT, the internal rotation of one methyl internal rotor caused splittings of all rotational transitions into A-E doublets, while internal rotations of the two non-equivalent methyl groups in 24DMTA into quintets. In addition, the microwave spectrum includes quadrupole hyperfine splittings caused by the ^{14}N nitrogen nucleus, making spectrum analysis more challenging. The programs *XIAM* and *BELGI*-C$_s$-*hyperfine* were used to deal with the relatively low methyl torsional barrier of 105.79(13) cm^{-1} found for MVT. The A and E torsional species were fitted separately to check the correctness of the assignment. For 24DMTA, the spectrum analysis was difficult due to the very low torsional barrier of 22 cm^{-1} of the methyl group adjacent to the sulfur atom. An intermediate torsional barrier of around 397 cm^{-1} was obtained for the methyl group adjacent to the nitrogen atom. The experimental results are compared with the predicted values obtained by quantum chemical calculations.



24DMTA



MVT

Spectroscopy on the first excited torsional state of propylene oxide

P. Stahl[1], B. E. Arenas[2,5], O. Zingsheim[3], M. Schnell[2,5], L. Margulès[4], R. A. Motiyenko[4], T. F. Giesen[1], G. W. Fuchs[1]

[1]Institute of Physics, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany, [2] Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany, [3]I. Physikalisches Institut, Universität zu Köln, [4]Université de Lille, Laboratoire de Physique des Lasers, Atomes et Molécules (PhLAM), 2 Avenue Jean Perrin, 59650 Villeneuve-d'Ascq, France, [5]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 1, 24118 Kiel, Germany

The chiral molecule propylene oxide, $CH_3C_2H_3O$, has been investigated at frequencies between 75–950 GHz using chirped-pulse Fourier-transform emission and conventional absorption spectroscopy. We studied the first excited vibrational mode, ν_{24}, corresponding to the torsional motion of the methyl group. The analysis was done using the internal rotation programs ERHAM and XIAM. Rotational constants and tunnelling parameters were derived, and the A-E splittings due to internal rotation were determined. The potential barrier height to internal rotation, V_3, was determined to be V_3=898.6611(894) cm^{-1}. Our results are compared with quantum chemical calculations and literature values. The implications of these measurements concerning astrophysical searches of vibrationally excited propylene oxide will be discussed.

IR ROTATIONAL SPECTRUM OF METHYLAMINE

I. Gulaczyk[1], M. Kręglewski[1]

[1]Faculty of Chemistry, Adam Mickiewicz University

Methylamine is considered a model molecule exhibiting two large amplitude motions: CH_3 internal rotation and NH_2 inversion. These two large amplitude motions are strongly coupled and give rise to a rich rotation-inversion-torsion structure in the vibrational states.

In the current work a recent progress is reported on assignment and fitting the pure rotational spectrum of methylamine in the ground vibrational state and in the first and the second torsional states. It was possible to assign in the IR spectrum the complete ^rR and ^rQ series for higher values of K and J, for all symmetry species.

The high resolution IR spectra were recorded in the range 40-360 cm^{-1} with a resolution of 0.00125 cm^{-1} using Bruker IFS-120HR spectrometer at the University of Oulu. About 8300 new infrared rotational transitions have been assigned in the ground, first and second torsional states using an original Loomis-Wood program dedicated to methylamine [1].

For each vibrational state a joint fit of rotational transitions of all symmetry species has been carried out. The transitions assigned in this project and published earlier were fit to a single state model based on the group theoretical formalism of Hougen and Ohashi [2]. The standard deviation of the fit for the ground state with $K \leq 20$ and $J \leq 50$ to 78 parameters was 0.00031 cm^{-1}. The standard deviation of the fit for the first excited state with $K \leq 20$ and $J \leq 45$ was 0.00066 cm^{-1} and 89 parameters were necessary. For the second excited torsional state with $K \leq 14$ and $J \leq 40$ and with 95 parameters a standard deviation of 0.00207 cm^{-1} was obtained. Only for the ground state the standard deviation is close to the experimental accuracy.

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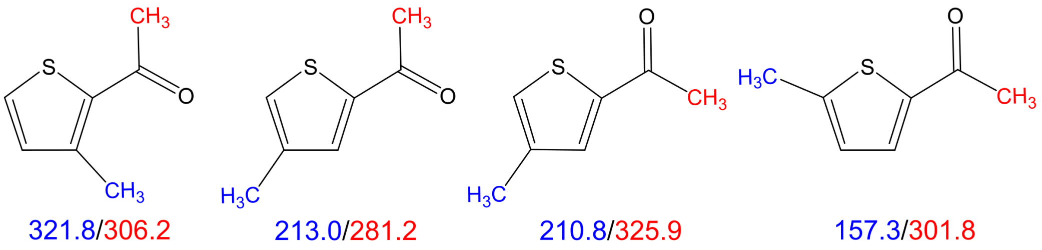
The effects of two inequivalent internal rotations in acetylmethylthiophenes explored by microwave spectroscopy

C. Dindic[1], L. Nguyen[2]

[1]Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany, [2]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7583, Université Paris-Est Créteil, Université de Paris, 61 avenue du Général de Gaulle, F-94010 Créteil, France

The microwave spectra of three isomers of acetylmethylthiophene were recorded using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2.0 to 26.5 GHz. Quantum chemical calculations predicted two stable conformers for all isomers, possessing either a *syn*- or an *anti*-orientation of the acetyl group. Both conformers were experimentally observed for 2-acetyl-4-methylthiophene (2A4MT, molecule (**2**) in Figure 1), while the spectra of the other two isomers showed exclusively transitions belonging to one conformer; *anti* in the case of 2-acetyl-3-methylthiophene (2A3MT, molecule (**1**) in Figure 1) and *syn* in the case of 2-acetyl-5-methylthiophene (2A5MT, molecule (**3**) in Figure 1).

Due to the internal rotation of the acetyl methyl and the ring methyl groups all rotational transitions split into five torsional species. These splittings could be resolved and analyzed for all assigned conformers, yielding the torsional barriers given in Figure 1. The impact of the substitution position where the methyl internal rotor attached to the aromatic thiophene ring and the relatively constant torsional barrier around 300 cm^{-1} of the acetyl methyl rotor will be discussed.



(**1**) *anti*-2A3MT (**2a**) *anti*-2A4MT (**2b**) *syn*-2A4MT (**3**) *syn*-2A5MT

Figure 1: Experimentally observed conformers of the three acetylmethylthiophene isomers. The torsional barriers of the acetyl methyl (red) and ring methyl (blue) groups are given in cm^{-1}.

Analysis of the low torsional barrier of a heavy C3v top: the case of trifluroacetic acid

L. Zou[1], R. A. Motiyenko[1], L. Margulès[1]

[1]Universite de Lille, Laboratoire PhLAM UMR 8523 CNRS

Trifluoroacetic acid (TFA, CF3COOH) is the final degradation product of many hydrochlorofluorocarbons, hydrofluorocarbons, and hydrofluoroolifines in the troposphere. The CF3 internal rotor is a heavy C3v top that strongly couples with the overall rotation of the molecule ($\rho = 0.68$). Despite the low torsional barrier of about 230 cm^{-1}, the high mass of the top leads to low tunneling probability in the ground state. The A-E splitting is not observable in the ground state rotational spectrum even using molecular beam Fourier transform microwave spectroscopy which typical resolution is few kHz[1]. In previous studies, the splitting was observed only for the v_t=4 excited torsional state[2], whereas the rotational lines for the v_t=1-3 states were not well measured. The missing lines from the v_t=1-3 states lead to the question of what the exact torsional barrier is, and in which state the tunneling splitting becomes observable. We perform a new global analysis of the TFA v_t=0-4 states with new spectral measurements from 50 to 330 GHz, and from 1.2 to 1.5 THz. In our data set, the tunneling splitting is observed for v_t=4 lines, and a small portion of v_t=3 lines. Our analysis was performed using the rho-axis method and RAM36 code. This joint analysis of five torsional states resulted in accurate determination of the V3 and V6 potential energy terms. The latest results will be presented.

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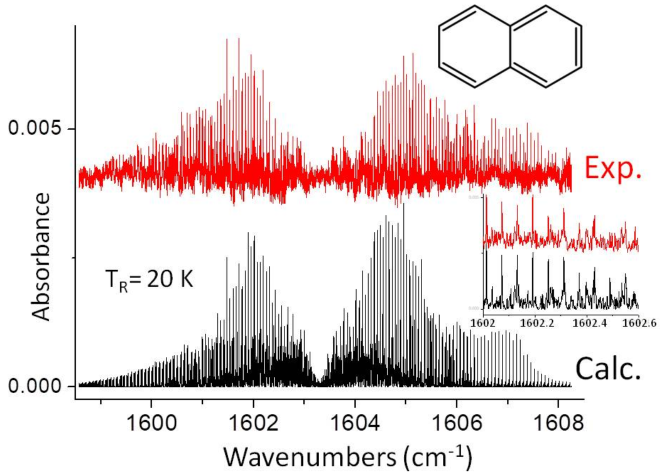
Parallel Session: Infrared, Contributed Talk (15min) **CB1**

High resolution rovibrational spectroscopy of bicyclic aromatic hydrocarbons.

S. CHAWANANON[1], P. ASSELIN[1]

[1]Laboratory MONARIS UMR 8233 CNRS, Sorbonne Université, Paris, FRANCE

Benzene dissociation from the UV and soft X-ray emission of proto-planetary nebula CRL618 [1] as well as the detection of Buckminsterfullerene (C_{60}) founded in meteorites [2] inquiry us how these large molecules were formed in the Interstellar medium (ISM). Since 80s, Polycyclic aromatic hydrocarbon (PAH) molecules are suspected to be the carriers of Unidentified Infrared Bands (UIB) emitted in the ISM but no unambiguous proof was provided until the recent discovery of benzonitrile [3] and cyano-naphthalenes [4] by radio-astronomy which confirms the interstellar PAH hypothesis. Feeding high resolution laboratory data about these compounds becomes highly necessary in the perspective of the future launch of James Webb Spatial Telescope, in order to elaborate chemical models leading to the formation of these molecular bricks. In this context, high-resolution IR jet-cooled experiments were realized with the SPIRALES set-up implemented at MONARIS. Three tunable quantum cascade lasers were used to investigate the 980-1030 cm $^{-1}$ and 1580-1720 cm^{-1} ranges of CH in-plane bending and CC ring stretch vibrational modes, respectively. The present study is firstly dedicated to smallest bicyclic PAHs, naphthalene and biphenyl. Their centro-symmetry excludes any pure rotation study and IR spectroscopy becomes mandatory to retrieve rotational parameters in both ground and excited vibrational states. Additionally, nitrogen-substituted polycyclic PAHs such as quinoline and isoquinoline have been investigated because of the assumed key role in the interstellar chemistry [6].



Jet-cooled laser spectrum of the CC ring stretch band of naphthalene compared to the simulated spectrum at a rotational temperature of 20 K.

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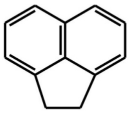
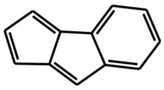
Acetylene loss from anthracene and phenanthrene cations

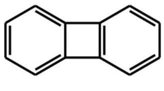
S. Banhatti[1], D. Rap[2], H. Leboucher[3], A. Simon[4], G. Wenzel[5], C. Joblin[6], B. Redlich[2], S. Schlemmer[1]*, S. Brünken[2]*

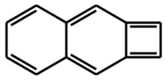
[1]I. Physikalisches Institut, Universität zu Köln, [2]FELIX Laboratory, Radboud University, [3]Laboratoire de Chimie et Physique Quantiques (LCPQ), [4]Laboratoire de Chimie et Physique Quantiques LCPQ/IRSAMC, [5]Aarhus University, [6]Institut de Recherche en Astrophysique et Planétologie (IRAP)

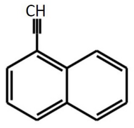
Polycyclic aromatic hydrocarbons (PAHs) are believed to be the carriers of the ubiquitous aromatic infrared bands observed in the spectra of galactic and extra-galactic astronomical sources. These PAH IR emissions are caused by the absorption of UV photons originating from astronomical sources and subsequent infrared emission due to molecular relaxation[1]. The processing of PAHs by UV photons also leads to their fragmentation, which has been recognized in recent years as an alternative route to the generally accepted bottom-up chemical pathways for the formation of complex hydrocarbons in UV-rich interstellar regions[2][3]. Here we study one such fragmentation process, the loss of acetylene from the anthracene and phenanthrene ($C_{14}H_{10}$) molecules after electron impact ionization, resulting in a fragment ion with the chemical composition $C_{12}H_8^+$. The dissociation product is expected to have many possible structures shown in the image. By employing the sensitive action spectroscopic scheme of infrared pre-dissociation (IRPD) in a cryogenic ion trap instrument coupled to the free electron lasers at the FELIX Laboratory[4][5], we have recorded the broadband and narrow line-width gas phase infrared spectra of the fragment ion ($C_{12}H_8^+$) formed by dissociative ionization of the two precursor PAHs ($C_{14}H_{10}$), and also the reference spectra of three low energy isomers of $C_{12}H_8^+$. Using DFT calculations at the B3LYP 6-311G(d, p) level of theory we have identified the dominant structure of the fragment isomers formed in the dissociation process. Molecular dynamics simulations (SCC-DFTB) will be presented in order to elucidate the fragmentation process.


Acenaphthylene: AcN⁺

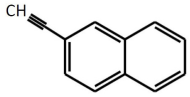

Benzopentalene: BP⁺


Biphenylene: BPh⁺


Cyclobuta[b]naph- thalene: CyN⁺



1-Ethynylnaph- thalene: 1-EN⁺



2-Ethynylnaph- thalene: 2-EN⁺

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Structure and dynamics of the semirigid HHe_2^+ and the fluxional HHe_3^+ cations

I. Simkó[1], F. Brieuc[2], C. Schran[2,4], T. Szidarovszky[1], C. Fábri[1], O. Asvany[3], A. G. Császár[1], D. Marx[2]*, S. Schlemmer[3]*

[1]Institute of Chemistry, ELTE Eötvös Loránd University, H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary, [2]Lehrstuhl fuer Theoretische Chemie, Ruhr-Universitaet Bochum, 44780 Bochum, Germany, [3]I. Physikalisches Institut, Universität zu Köln, [4]Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

The HHe_n^+ cationic complexes consist of a strongly-bound linear HHe_2^+ chromophore surrounded by weakly-bound solvating He atoms. The structures and the vibrational dynamics of the HHe_n^+ (n=3-6) complexes have been previously investigated using action-spectroscopic experiments in a cryogenic ion-trap machine and high-level electronic-structure computations [1-3]. In these previous studies, the anharmonic frequencies for the vibrations of the chromophore have been computed using perturbation theory, resulting in a reasonable agreement with experiment. Understanding the large-amplitude motions of the weakly-bound solvating He atoms requires variational nuclear-motion computations. Based on neural-network potential energy surfaces (NN-PES) [4-5] developed as part of this study, we determined rovibrational energies of HHe_2^+ and HHe_3^+ using the GENIUSH code [6-8]. The training set of the NN-PES consist of CCSD(T*)-F12b/AVQZ computations for configurations sampled within an active learning framework from path integral molecular dynamics simulations [5]. For HHe_2^+, the computed rovibrational transitions corresponding to the asymmetric stretch show outstanding agreement with experiment, demonstrating the excellent quality of the NN-PES. In the case of HHe_3^+, the third, solvating He orbits around the HHe_2^+ unit forming a torus. We studied the shape of the fluxional HHe_3^+ cation and its vibrations involving the solvating He atom, both with and without the consideration of the permutational symmetry of the He atoms. We identified the bending and stretching modes of the solvating He atom, as well as states corresponding to a linear secondary minimum structure. Visualization of the vibrations and the temperature-dependent dynamical structure of the cation is helped considerably by computing and plotting the nuclear density.

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Oxygen B-band P-branch study: simultaneous observation of Dicke narrowing and speed-dependence effects

A. A. Balashov[1,2], K. Bielska[1], J. Domysławska[1], S. Wójtewicz[1], M. Słowiński[1], M. Piwiński[1], A. Cygan[1], R. Ciuryło[1], D. Lisak[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziadzka 5, 87-100 Torun, Poland, [2]Institute of Applied Physics of the Russian Academy of Sciences, Ulyanov str. 46, 603950 Nizhny Novgorod, Russia

Oxygen is one of the two most abundant molecular gases in the terrestrial atmosphere. B band is the second most intense band in the red part of the absorption spectrum of the O_2 molecule. It is less commonly used for the remote sensing of the atmosphere mainly because the B-band intensity is about 15 times lower than the A-band. Until recently another limiting factor was the lack of accurate laboratory data. Accurate reference data, including full sets of line-shape parameters, is necessary for multiple atmospheric applications, in particular, accurate determination of the pressure and temperature profiles [1] across the atmosphere and improved parameters of clouds such as their top height [2].

In this study, we measured line-shape parameters of three transitions from the P branch. In contrast to the previous study [3], we simultaneously observe the speed-dependence of the collisional broadening and the Dicke narrowing effect [4], as well as the line asymmetry due to the speed-dependence of the collisional shifting for the pressures down to 1.1 kPa. It became possible due to the significantly increased spectra signal-to-noise ratio. The measurements were done with two experimental techniques: well-established cavity ring-down spectroscopy (CRDS) [5] and cavity mode-width spectroscopy (CMWS) [6,7] that allowed us a more reliable estimation of the determined line-shape parameters systematic uncertainties. The unperturbed line positions are determined within 40 kHz and the line intensities at 0.2% level. New results are compared with our previously published data [3] of the P-branch measurements and observed systematic deviations on the line intensities are explained.

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Satellites in Infrared and Raman Spectra of Linear Molecules

A. P. Kouzov[3], A. V. Sokolov[1], N. I. Egorova[2]

[1]Saint Petersburg State University, Universitetskaya emb., 7/9, 199034 Saint Petersburg, Russia, [2] St. Petersburg University of State Fire Service of Emercom of the Russian Federation, St. Petersburg, 196105 Russia, [3]Saint Petersburg State University, Universitetskay

A nonMarkov theory of diffuse satellites appearing around the allowed resonance rotational lines perturbed by monoatomic buffer gases is expounded. As the buffer-gas pressure grows, the lorentzian mother lines adjacent to the band origin become attenuated because of the intensity transfer to surrounding satellites. Different channels contributing to the attenuation effect of infrared and Raman lines of linear molecules are considered. The calculated attenuation coefficients reasonably agree with experimental data available for HCl and HF absorption spectra perturbed by noble gases [1-3]. .Based on the nonMarkov dynamical theory, the satellite formation in the allowed spectra of dense media consisting of linear molecules is treated. In this case, coupling of the rotational transitions in neighbouring molecules results in the appearance of satellites at the combination frequencies.

Support from the Russian Foundation for Basic Research (grant 19-03-00830) is gratefully acknowledged.

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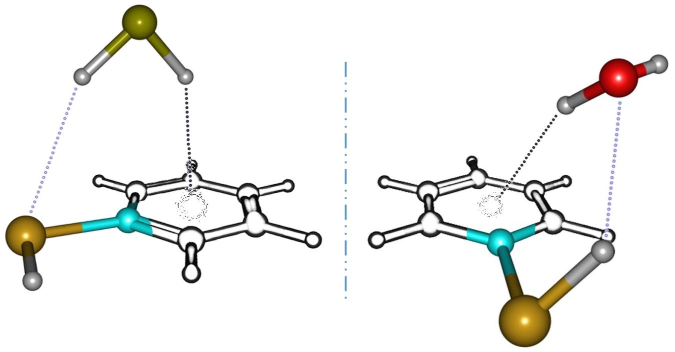
Observation of Selenium-centered Hydrogen Bonds by Jet-Cooled Microwave Spectroscopy: Benzeneselenol ··· H_2O vs. Benzeneselenol ··· H_2S

M. Juanes[1], R. T. Saragi[1], R. Pinacho[2], M. Jaraíz[2], A. Lesarri[1]

[1]University of Valladolid, Departamento de Química Física y Química Inorgánica, Facultad de Ciencias – I.U. CINQUIMA (Spain), [2]University of Valladolid, Departamento de Electrónica, ETSIT (Spain)

Despite the importance of selenium in our daily lives (selenium is interesting because it is simultaneously toxic but essential for humans to produce proteins), the number of high-resolution spectroscopic studies of selenium-centered hydrogen bonds (HBs) is very small. Moreover, from a fundamental point of view it is interesting to compare the selenium HBs with those made by other chalcogen atoms (such as oxygen and sulfur). Selenium-centered HBs can be studied in weakly-bound intermolecular complexes isolated in a jet expansion. Here we report on the dimers of benzeneselenol ··· H_2O and benzeneselenol ··· H_2S, probed in a supersonic jet using chirped-pulsed and cavity Fourier-transform microwave spectroscopy in the cm-wave region 2-18 GHz. Notable differences have been observed in the behavior of the two selenol dimers. In the benzeneselenol monohydrate the selenol group acts as proton donor to water. Conversely, in the hydrogen sulfide dimer the selenol accepts a proton from the sulfide. The spectrum of several monosubstituted isotopologues were also assigned, including those of selenium, $H_2{}^{18}O$ and $H_2{}^{34}S$, which were used to calculate ground-state effective structures and HB structures in both cases. Accurate rotational parameters and density-functional-theory supporting calculations will be reported for the investigated species.



Investigation of collisional effects in molecular spectra - accurate ab initio calculations in HD-He system

K. Stankiewicz[1], H. Jóźwiak[1], M. Gancewski[1], N. Stolarczyk[1], F. Thibault[2], P. Wcisło[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, Toruń, 87-100, Poland, [2] CNRS, IPR (Institut de Physique de Rennes)-UMR 6251, F-35000 Rennes, France

The abundance of molecular hydrogen and atomic helium in the universe makes them an important system to study in various fields. A mixture of molecular hydrogen and helium is the main component of the atmospheres of gas giants in the Solar System and is predicted to be a dominant constituent of the atmospheres of some types of exoplanets [1]. The hydrogen molecule is also the simplest molecule, the structure of which can be calculated from first principles, which makes it well suited for accurate tests of ab initio calculations. In particular, HD molecule, despite its lower abundance than H_2 isotopologue is noticeable in spectroscopic studies due to the presence of its dipole moment even in the electronic ground state. Moreover, studies of the H_2–rich atmospheres are well suited for measuring the D/H ratio, which is crucial for understanding the evolution of the Universe and planets' atmospheres [2, 3]. Studies show [4] that in some cases the uncertainty of astronomical observations of hydrogen molecule spectra is dominated by the uncertainties of collisional parameters, including pressure broadening and pressure shift coefficients. An accurate list of the line–shape parameters is necessary for a correct interpretation of molecular spectra from the atmospheres of gas giants [4] and exoplanets [5].

We present the methodology and results of ab initio calculations of collisional effects for 12 purely rotational and 60 rovibrational electric dipole transitions in R and P branches: from R(0) to R(5) and from P(1) to P(6) in the 0–0 to 5–0 vibrational bands. We used state-of-the-art potential energy surface [6] - an improved version of the one reported by Bakr, Smith, and Patkowski [7]. We also carefully examined the validity of the usually assumed approximation for rovibrational transitions - centrifugal distortion neglection - in the case of the HD-He system. Available experimental studies [8][9] are in good agreement with our calculations for most transitions, however, some of the results are beyond the estimated uncertainty. The experimental values for rovibrational lines only consist of $R_1(0)$ and $R_1(1)$ transitions at 77 K. This, together with the fact that the measurements were using less accurate line-shape models, and current experimental techniques are more accurate, show that there is a strong need for new accurate experimental studies of collisional line-shape parameters.

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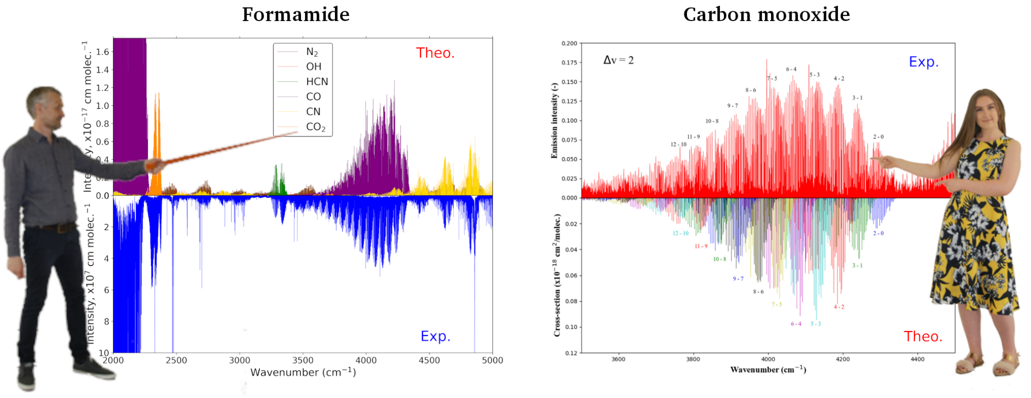
Calculating the non-LTE spectra of small molecules using the ExoMol Database

V. H. Clark[1], S. N. Yurchenko [1]*

[1]Department of Physics and Astronomy, UCL, London, WC1E 6BT, UK

Our new methodology [1] for calculating the non-LTE line lists of small molecules using the ExoMol Database (www.exomol.com) [2] is presented here, and compared against experimentally obtained spectra. We use a simplistic 1D approach based on the Harmonic approximation to model the intensity pattern of the Δv = 1 and the Δv = 2 bands of $^{12}C^{16}O$ experimental spectra. We achieve this by simulating the corresponding non-LTE vibrational populations of CO produced by formamide glow discharge [3]. We also demonstrate that our 1D model can be used for the full formamide discharge spectra between 2000 cm^{-1} – 5000 cm^{-1}, and can model spectra containing up to six non-LTE molecules; including linear and non-linear triatomics, and both hetero- and homodiatomics. Excellent agreement with experiment is achieved in both cases.



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A Quantum Chemical Method Producing Accurately Predicted Barrier Heights to Methyl Group Internal Rotation - The Test Case of Acetylspecies

K. G. Lengsfeld[1], P. Buschmann[1], F. Dohrmann[1], A. Sander[1], J. Grabow[1]*

[1]Institut für Physikalische Chemie und Elektrochemie

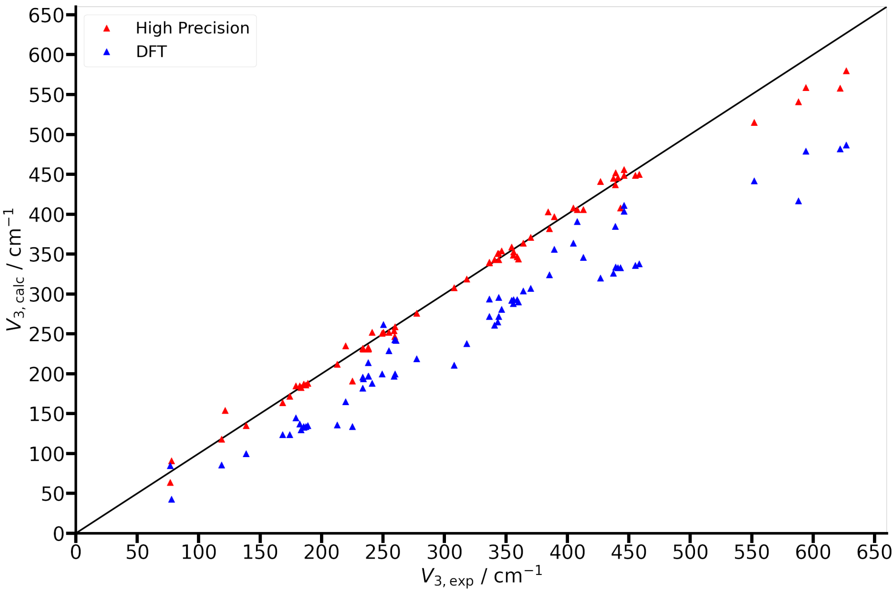
The analysis of the internal dynamics in molecules is intriguing not only for spectroscopists but also many other disciplines of physical chemistry like thermodynamics and quantum chemistry. The shape and magnitude of the threefold hindering potential corresponding to the internal molecular rotation of methyl groups, analogous to the interaction of molecular rotation with nuclear spins of atoms with a permanent nuclear quadrupole moment, is reflected in the fine and hyperfine structure of high-resolution rotational spectra. A corresponding (re)analysis allows characterizing the methyl group large amplitude motions, which can also serve as an intramolecular sensor for (stereo)electronic effects. Furthermore, for an efficient analysis of the spectral fine structure, good quantum chemical predictions of the barrier heights are significant.

Therefore, the reproducibility of the experimentally determined barrier heights of 69 molecules containing an acetyl group was tested using a promising combination of quantum chemical methods.

In addition to a mean deviation of only 2.9 % resulting from Fig. 1, an empirical scaling factor for simple density functional theory calculations could be determined, which caused a significant improvement of this simple method.

Thus, predictions by both methods can be utilized as standard procedure for the prediction of molecules not previously characterized by rotational spectroscopy.

Conclusively, the found acetylmethyl barrier heights of different carboxylic acid derivatives can be correlated with their reactivity.



High-Level Ab Initio Quartic Force Fields and Spectroscopic Characterization of C_2N^-

C. M. Rocha[1], H. Linnartz[1]*

[1]Laboratory for Astrophysics, Leiden Observatory, Leiden University, P.O. Box 9513, NL-2300 RA
Leiden, The Netherlands

Although the existence and importance of negative molecular ions had been conjectured in the early days of astrochemistry, it was not until 2006 that the first interstellar anion, C_6H^-, was finally detected. This led to a resurgence of interest of chemists, physicists, and astrophysicists in anions, motivating new surveys as well as theoretical and laboratory studies. As a result, several other negatively charged species were soon identified like C_4H^-, C_8H^-, C_3N^-, C_5N^- and CN^- [1]. Assuming electron radiative attachment (REA) as their major formation route, previous anion astrochemical models have been successful in reproducing the observed abundances of the larger, highly-dipolar carbon-chain anions like C_8H^-, C_6H^-, and C_5N^-. However, for the smallest anionic species (*e.g.*, CN^- and C_3N^-) for which REA to their parent neutrals are theorized to very slow, notable discrepancies have soon appeared between the modeled and observed anion-to-neutral ratios [1], suggesting that other alternative pathways might dominate their synthesis [2]. Recent laboratory studies by Chacko et al. [3] pointed out the dominance of the (as yet unobserved) C_2N^- species as fragmentation product of larger carbonitrile anions in UV-abundant circumstellar media, thereby offering new prospects into its omnipresence in the external layers of the carbon-rich star IRC+10216. Motivated by these most recent findings and the general lack of spectral signatures of this anion, in this talk, I will discuss our most recent efforts to obtain accurate rovibrational spectroscopic constants and anharmonic vibrational frequencies for l-C_2N^-($^3\Sigma^-$) and c-CNC($^1A_1$) by means of a high-level theoretical approach. Special attention will be paid into the characterization and computation of their quartic force fields (QFFs) [4,5] using state-of-the-art electronic structure composite methods followed by nuclear motion calculations. It is then expected that the new spectroscopic data here reported prompt future high-resolution laboratory and observational studies on this target molecular anion.

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Unveiling the Shape of neutral Levodopa

M. Sanz-Novo[1], Í. León[1], E. R. Alonso[2,1], J. L. Alonso[1]*

[1]Universidad de Valladolid / Departamento de Química Física y Química Inorgánica, [2]Universidad del País Vasco (UPV-EHU)

Neurotransmitters are specific molecules involved in the transmission of neural signals between neurons. The study of the shape of neurotransmitters and their most essential precursors is of great relevance to biochemistry since it plays a key role in the molecular recognition process at the receptor site. We here report the first rotational study of neutral levodopa, an aminoacid precursor of neurotransmitters dopamine [1], adrenaline and noradrenaline using a combination of broadband chirped pulse FTMW spectroscopy and a laser ablation vaporization system (LA-CP-FTMW). Three distinct conformers of levodopa have been unambiguously identified in the supersonic jet. Also, we have analyzed the ^{14}N nuclear quadrupole hyperfine structure to identify and experimentally establish the intramolecular interactions in which the N-bearing functional group is involved, showing the existence of stabilizing N-H-π interactions for the observed structures.

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Energy-Corrected Sudden approach to the non-Markovian relaxation matrix for two linear colliders

A. V. Sokolov[1], J. Buldyreva[2], A. P. Kouzov[1]

[1]Saint Petersburg State University, [2]Institut UTINAM, UMR CNRS 6213

A finer picture of collisional effects on spectral band shapes is urgently demanded by a number of atmospheric and combustion explorations [1]. For that, simulations of band profiles in large spectral intervals should be done at various thermodynamic conditions, in particular for elevated gas densities where the line-mixing effects are strongly pronounced. The problem is solved when the fundamental, frequency-dependent relaxation (super)matrix Γ(ω) is known. Presently, the only affordable receipt to calculate Γ(ω) without limitations of the perturbation theory is due to the Energy- and Frequency Corrected Sudden Approximation (EFCSA) model developed initially for the structureless bath [2] and extended recently to linear perturbers [3], assuming collision durations to be finite, yet much shorter than the period of collider's rotation.

In a previous study [4], we suggested an approach based on spectral moments to model the translational interaction spectral functions (ISF). This approach requires, however, refined potential energy surfaces available only for a limited number of molecular systems. To make non-Markovian calculations feasible for an arbitrary molecular pair, we develop here a semi-empirical approach to ISF simulation based on the Energy-Corrected Sudden model. While there exist papers presenting ECS-modeling of the Markovian relaxation matrix for a linear perturber [5] or the non-Markovian ECS matrix for a structureless perturber [6], to our knowledge, there is no published work describing non-Markovian relaxation matrices that accounts for the anisotropy of the perturbing molecule.

After having applied the basic hypotheses of the ECS approximation and having factorized the ISFs into frequency- and anisotropy-dependent parts, we consider the particular case of the isotropic Q-branch, which allows identification of the frequency-dependent factor with the adiabaticity factor and enables relating the anisotropy-dependent factor to the bimolecular transition rates. We propose various analytical multi-parameter models for bimolecular basic transition rates that are used, together with a Lorentzian-type adiabaticity factor, for ISF modeling and are shown, on the example of high-pressure anisotropic Raman spectra of nitrogen, to be suitable for theoretical prediction of large-band spectra of dense gases of linear molecules.

AS and AK acknowledge the financial support from the RFBR (project number 19-33-90244).

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Program, Tuesday, August 31, 2021

	Mini-Symposium: Precision Spectroscopy (D) Chair: Paolo de Natale, Istituto Nazionale di Ottica, Italy
11.30	***Stephan Schiller***, Heinrich-Heine-Universität Düsseldorf «High-resolution spectroscopy of the simplest molecule: from novel techniques for molecular ion spectroscopy to fundamental physics»
12.00	***Takeshi Yasui***, Tokushima University «THz Dual-Comb Spectroscopy»
12.30	***Shui-Ming Hu***, University of Science and Technology of China «Cavity-enhanced precision spectroscopy of molecules: methods and applications»
13.00	***Luigi Consolino***, Istituto Nazionale di Ottica INO-CNR, Florence «Terahertz Frequency Metrology»
13.30	Break
	Invited Lectures (E) Chair: Jean vander Auwera, Université Libre de Bruxelles, Belgium
14.00	***Joseph T Hodges***, National Institute of Standards and Technology «Probing the dynamic response of a ring-down cavity with heterodyne detection to measure sample absorption and dispersion»
14.45	***Ann Carine Vandaele***, BIRA-IASB «Spectroscopic Exploration of the Martian System»
15.30	Break
16.00	**Poster Session 2** Watch the short video presentations Meet the poster presenters on the interactive platform MeetAnyway
17.30	End of day 3

High-resolution spectroscopy of the simplest molecule: from novel techniques for molecular ion spectroscopy to fundamental physics

S. Schiller[1]

[1]Institut für Experimentalphysik, Heinrich-Heine-Universität Düsseldorf, Germany - step.schiller@hhu.de

Molecular hydrogen ions (MHI), the simplest molecules, are three-body quantum systems composed of two simple nuclei and one electron. They are of high interest for fundamental physics because, in contrast to the hydrogen atom family, their internal energy depends not only on the electron-nucleus interaction but also on the nucleus-nucleus interaction and on the nuclear masses. The relative simplicity of MHIs allows predictions by ab initio theory, that as of today has reached an impressive precision approaching that of the hydrogen atom theory. The experimental study of the MHI poses its own challenges.

Over the years, we have developed a set of techniques for the precise study of molecular ions at different levels of resolution and precision. They rely firstly, on trapping MHI in a linear ion trap and sympathetic cooling by co-trapped and laser-cooled beryllium ions, allowing reaching kinetic energies of the order 10 mK [1].

A breakthrough in resolution and precision was achieved by introducing novel Doppler-free spectroscopy techniques for ensembles of molecules, rather than single molecules. For rotational spectroscopy we interrogate a prolate ion ensemble and irradiate the spectroscopy wave along the small width, achieving the Lamb-Dicke regime. For vibrational transitions (5 µm) we work with ensembles so small that the ions arrange in a string-like fashion on the trap axis. Again, irradiation of the spectroscopy laser is performed orthogonally to the trap axis. Under these conditions we observed one-photon electric-dipole transitions with resolved carrier. Line resolution as high as 3×10^{11} and transition frequency uncertainties as low as 3×10^{-12} were achieved with HD^+ [2,3].

The measured rotational and vibrational frequencies are in agreement with their predicted values, when CODATA fundamental constants are used as input to the predictions. Assuming the correctness of the predictions within their estimated theoretical uncertainties, we determined values of the ratio of reduced nuclear mass and electron mass. Their uncertainties are competitive with the best direct determinations using Penning trap mass spectroscopy. Further, an upper limit for the strength of a hypothetical fifth force between the two nuclei could be set that was by more than one order lower than deduced from previous experiments.

Finally, the resolution and precision of the rotational spectroscopy is so high that we could determine the tiny quadrupole moment of the deuteron to percent precision [2].

Recent developments in the techniques will be presented.

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THz Dual-Comb Spectroscopy

T. Yasui[1]

[1]Tokushima Univ.

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Optical frequency combs are innovative tools for broadband spectroscopy because a series of comb modes can serve as frequency markers that are traceable to a microwave frequency standard. However, a mode distribution that is too discrete limits the spectral sampling interval to the mode frequency spacing even though individual mode linewidth is sufficiently narrow. Here, using a combination of a spectral interleaving and dual-comb spectroscopy in the terahertz (THz) region, we achieved a spectral sampling interval equal to the mode linewidth rather than the mode spacing. The spectrally interleaved THz comb was realized by sweeping the laser repetition frequency and interleaving additional frequency marks. In low- pressure gas spectroscopy, we achieved an improved spectral sampling density of 2.5MHz and enhanced spectral accuracy of 8.39x10^−7 in the THz region. The proposed method is a powerful tool for simultaneously achieving high resolution, high accuracy, and broad spectral coverage in THz spectroscopy.

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Cavity-enhanced precision spectroscopy of molecules: methods and applications

S. Hu[1]

[1]Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, 230026 China

Precise determination of ro-vibrational transition frequencies of molecules are interested in various studies such as molecular dynamics, metrology, astronomy, and fundamental physics. However, the accuracy of most line positions in the near infrared is limited to 10^{-3} - 10^{-4} cm^{-1} (~ 1 MHz) due to broadening (Doppler and collision induced) and/or the weakness of overtone transitions. Here we introduce cavity-enhanced spectroscopy methods we developed for precision spectroscopy of molecules. Using high-finesse cavities, we demonstrate a detection sensitivity (noise-equivalent absorption coefficient) of 10^{-12}/cm and a frequency accuracy of 1 kHz [1]. Two-color double resonance (DR) spectroscopy using continuous-wave diode lasers [2] is also demonstrated, which allows us to probe highly-excited states of molecules with unprecedented accuracy. A few application examples will be given, including kHz-accuracy measurements of the (30012) and (60025) bands of CO_2 [3], and the unexpected "distorted" line profile of the Lamb-dip spectrum of HD [4,5].

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Terahertz Frequency Metrology

L. Consolino[1]

[1]Istituto Nazionale di Ottica INO-CNR, Largo E. Fermi 6, Florence, Italy I-50125

In the last few decades, the THz window of the electromagnetic spectrum has emerged as enabling breakthrough scientific and technological applications in such diverse fields as information and communications technology (ICT), biomedicine, homeland security, quality control of food and global environmental monitoring. Likewise, high precision THz spectroscopy of rotational and ro-vibrational molecular transitions promises to deliver many novel physical insights. In this framework we will report on two different approaches for THz metrological-grade radiation, the first related to difference frequency generation (DFG) based broadband continuous wave (CW) THz source, the second regarding the characterization and applications of Quantum Cascade Lasers (QCL) based THz frequency combs (FCs).

1. DFG-based broadband CW THz source

Regarding THz frequency metrology, a lot of work as been done on single mode QCL setups. However, in order to fully exploit the potential of this key spectral region, the challenge is to merge, in a single source, three crucial aspects: an even broader spectral coverage towards higher THz frequencies (covered neither by QCLs nor by other traditional THz sources), metrological-grade performances (i.e. high resolution and accuracy with referencing to the primary frequency standard), power levels sufficient for room-temperature detection. In our work we demonstrate room-temperature generation and detection of continuous-wave THz radiation spanning three octaves in the THz range, from 1 to 7.5 THz, and performing high-accuracy molecular spectroscopy. This unprecedented result makes use of a simple, reliable approach that combines, in a unique set-up, robust telecom laser components with difference-frequency nonlinear generation.

In synthesis, the main contribution of our work is the combination of all the following aspects: i) room temperature CW generation, based on the fully-developed and commercial telecom fiber laser technology that grants a high level of compactness, stability and reliability to our new source; ii) a 3-octave spectral coverage, from 0.97 to 7.5 THz, that is obtained by the combined use of a Cherenkov emission scheme and strong light confinement in a surface nonlinear waveguide; iii) high power levels enabling both room temperature detection and high-precision THz spectroscopy, achieved thanks to a CW generation efficiency as high as 10^{-7} W^{-1} ; iv) frequency referencing to the primary frequency standard by means of a mode-locked femtosecond laser and a GPS disciplined Rubidium-Quartz oscillator; v) a state-of-the-art accuracy in the order of 10^{-9} obtained with a room temperature Golay cell detector. The proposed approach paves the way to a new class of metrological-grade sources spanning most of the THz range for countless demanding applications.

2. QCL-based THz frequency combs

The most common sources for FCs are mode-locked lasers, whose high level of coherence enabled a myriad of scientific applications, providing a frequency ruler for any laser emitting within their spectral range. For this reason huge efforts have been spent to extend the characteristics of FCs to all spectral regions, and to extend the figure of merits of FCs to other non-conventional comb-like source. In this framework Quantum Cascade Lasers (QCLs) technology, both in the mid-infrared and THz region, is exploiting the extraordinary versatility of these devices for developing active regions with engineered optical dispersion that emit optical frequency combs. Thanks to four-wave-mixing non-linear processes happening inside the active medium, proper mode-locking is obtained. The Fourier modal phases, ultimately describing comb operation are retrieved thanks to the Fourier Analysis of Comb Emission (FACE) technique, which confirms the high level of coherence of these sources, and enables retrieval of the temporal emission profile.

The metrological-grade performance of this class of devices is probed thanks to the full phase referencing to the primary frequency standard, achieving ~2 Hz in 1 s stability and ~6 Hz accuracy for the emitted modes. Independent and full control of the two comb degree of freedom is also demonstrated and characterized. Finally, application of a QCL-FC to high-accuracy molecular spectroscopy is shown in a hybrid dual-comb spectroscopy (DCS) setup [7]. The most

Probing the dynamic response of a ring-down cavity with heterodyne detection to measure sample absorption and dispersion

J. T. Hodges[1]

[1]Optical Measurements Group, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg Maryland, 20899, U.S.A

style="text-align: justify;">Most cavity ring-down spectroscopy applications involve measurements of single-mode intensity decay rates at zero frequency (dc). These decay rates are proportional to the total cavity intensity losses but are independent of dispersion effects. Notable exceptions include experiments using ac heterodyne beat signals between a local oscillator and cavity mode[1] or two cavity modes[2]. Building on this prior work, I will discuss a new heterodyne-detected cavity buildup/ring-down technique, collaboratively developed by D. Lisak and coworkers at Nicolaus Copernicus University (Torun, Poland) and members of the Optical Measurements Group at the National Institute of Standards and Technology (Gaithersburg Maryland, U.S.A.). This approach, referred to as dynamic mode-resolved heterodyne spectroscopy (DMHRS), yields the widths and positions of cavity modes to quantify sample absorption and dispersion, respectively. I will discuss how the cavity response can be described as a first-order linear system[3] in which mode fields are induced by driven or random variations in the probe laser amplitude and/or phase. Fourier analysis of heterodyne-detected buildup and decay signals yields spectrally distinct Lorentzian resonances caused by beating between probe-mode and local oscillator-mode fields. Importantly, all spectral information is encoded in terms of measured optical frequencies and radio frequencies, with strong immunity to amplitude variations, allowable frequency mismatch between probe and cavity, and no need for path length calibration. Specific examples and related work presented include cavity buildup spectroscopy[4] enabling measurements on time scales much less than the decay time, Cs-clock-referenced line positions in Doppler-broadened spectra[5] providing relative uncertainties at the 10^{-12} level for near-IR transitions of carbon dioxide, and parallel dual-comb cavity ring-down spectroscopy for broadband measurements of absorption and dispersion in methane[6].

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Spectroscopic Exploration of the Martian System

A. Vandaele[1], I. R. Thomas[1], S. Aoki[2], J. T. Erwin[1], L. Neary[1], A. Piccialli[1], L. Trompet[1], B. Vispoel[1], Y. Willame[1], S. Robert[3,4]*, F. Daerden[1]*

[1]BIRA-IASB, [2]ISAS, JAXA, Japan, [3]BIRA-IASB/UCLouvain, [4]Institute of Condensed Matter and Nanosciences, Université catholique de Louvain

Ann C. Vandaele (1), F. Daerden (1), S. Aoki (2), C. Depiesse (1), J. Erwin (1), L. Neary (1), A. Piccialli (1), S. Robert (1,3), I. R. Thomas (1), L. Trompet (1), S. Viscardy (1), B. Vispoel (1), Y. Willame (1)

(1) Royal Belgian Institute for Space Aeronomy (IASB-BIRA), Brussels, Belgium; (2) ISAS, JAXA, Japan; (3) Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Chemin du Cyclotron 2, 1348 Louvain-la-Neuve, Belgium (a-c.vandaele@aeronomie.be)

Mars and its two moons Phobos and Deimos have been scrutinized for decades using spectroscopic instruments operating in different wavelength ranges, at different spectral resolutions. After a brief description of what such instruments can teach us, we will focus on some recent results obtained by the NOMAD ("Nadir and Occultation for MArs Discovery") spectrometer suite on board the ExoMars Trace Gas Orbiter. This instrument has been designed to investigate the composition of Mars' atmosphere, with a particular focus on trace gases, clouds and dust. The instrument probes the ultraviolet and infrared regions covering large parts of the 0.2-4.3 µm spectral range [1,2], with 3 spectral channels: a solar occultation channel (SO – Solar Occultation; 2.3–4.3 µm), a second infrared channel capable of nadir, solar occultation, and limb sounding (LNO – Limb Nadir and solar Occultation; 2.3–3.8 µm), and an ultraviolet/visible channel (UVIS – Ultraviolet and Visible Spectrometer, 200–650 nm). The infrared channels record spectra at high spectral resolutions ($\lambda/d\lambda \sim 10,000–20,000$) provided by an echelle grating used in combination with an Acousto Optic Tunable Filter (AOTF) which selects the spectral region to be recorded. The sampling rate for the solar occultation measurement is 1 second, which provides high vertical sampling step (~1 km) and resolution (~2 km) from the surface to 200 km. Thanks to the instantaneous change of the observing diffraction orders achieved by the AOTF, the SO channel is able to measure five or six different spectral intervals per second in solar occultation mode. The UVIS channel has a spectral resolution

Since its arrival at Mars in April 2018, NOMAD performed solar occultation, nadir and limb observations dedicated to the determination of the composition and structure of the atmosphere. Since the beginning of operations, NOMAD acquired more than 4000 solar occultations with an almost complete coverage of the planet. Here we report on the different discoveries highlighted by the instrument during its first full Martian year of observations: investigation of the 2018 Global dust storm and its impact on the water uplifting and escape, on temperature and pressure increases within the atmosphere; dust and ice clouds distribution; ozone measurements; dayglow observations; detection of HCl vertical profiles and in general advances in the analysis of the spectra recorded by the three channels of NOMAD.

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Efficient compression of molecular line lists: application of 'super-energies' to the ExoMol database

X. Ke Lin[1], S. Wright[1], A. Owens[1], J. Tennyson[1], S. N. Yurchenko [1]*

[1]Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK (s.yurchenko@ucl.ac.uk)

A new compression algorithm for the efficient storage of molecular line lists is presented. The algorithm is based on the ‘super-energies’ approach recently developed and applied to produce a compact HITEMP line list for methane [1]. This method assumes a set of artificial lower state (super-)energies and corresponding reference intensities for an approximate description of the temperature dependent molecular absorption (absorption coefficient) on a grid of wavenumbers. The super-energies compression is then applied to the continuum part of the molecular spectrum.

Here we adopt and develop the HITEMP compression algorithm to be applicable to the ExoMol data format and generate new compressed line lists for SiO_2 [2], H_2O [3], KOH and NaOH [4]. A typical compression of a line list consisting of, e.g., 40 billions SiO_2 lines is compressed to about 40 million data points. Advantages and limitations of the ‘super-energies’ approach will be discussed. The compressed molecular line lists will be included in the ExoMol database (WWW.EXOMOL.COM) and their use should greatly facilitate atmospheric retrievals in exoplanets and other hot astronomical bodies.

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HITRAN2020 and remote sensing of the terrestrial atmosphere

I. E. Gordon[1], R. J. Hargreaves[1], L. S. Rothman[1], R. Hashemi[1], E. V. Karlovets[1], F. S. Skinner[1], E. K. Conway[1], A. A. Finenko[2,1], R. V. Kochanov[3,1]

[1]Center for Astrophysics, Harvard & Smithsonian, Atomic and Molecular Physics Division, Cambridge MA, USA, [2]Lomonosov Moscow State University, Moscow, Russia, [3]Tomsk State University, Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk, Russia

The HITRAN database is essential to the remote sensing of the terrestrial atmosphere. The new 2020 edition of the database will be presented. It is a coordinated effort that includes dozens of international experimentalists, theoreticians, atmospheric and planetary scientists who measure, calculate and validate the HITRAN data.

The lists for almost all of the HITRAN molecules in the line-by-line section were updated (and several additional molecules have been added) in comparison with the previous compilation HITRAN2016 [1]. The extent of these improvements range from updating a few lines of certain molecules to complete replacements of the lists and introducing additional isotopologues. Many new vibrational bands were added to the database, extending the spectral coverage and completeness of the line lists. Six new molecules were also added to HITRAN, including CH_3F, CS_2, CH_3I, and NF_3 that are all important for remote sensing. In addition, the accuracy of the parameters for major atmospheric absorbers has been increased, often featuring sub-percent uncertainties.

The number of parameters was also increased significantly, now incorporating, for instance, non-Voigt line profiles for many gases [2,3]; broadening by water vapor [4]; update of collision-induced absorption sets [5],to name a few.

The HITRAN2020 edition continues to take advantage of the new database structure and interface available at www.hitran.org [6] and through the HITRAN Application Programming Interface (HAPI) [7].The functionality of both tools has been extended for the new edition.

Some of the validation efforts will be demonstrated. Note, a parallel poster by R. Hargreaves regarding improvements concerning planetary atmospheres.

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Investigation of the plasma chemistry of phenanthrene and its mixture with acetonitrile using broadband rotational spectroscopy

D. Neidt[1,2], D. Loru[1], A. L. Steber[1], M. Schnell[1,2]*

[1]Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany, [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Straße 1, D-24118 Kiel, Germany

The interstellar formation and destruction processes of polycyclic aromatic hydrocarbons (PAHs), as well as their reactivity with other molecules of astronomical interest, are still far from being fully understood. A way to get insight into these processes in the laboratory is by combining electrical discharge sources with spectroscopic techniques.

In this respect, the electrical discharge chemistry of the PAH phenanthrene and its mixture with acetonitrile has been investigated by using chirped pulse Fourier transform microwave spectroscopy coupled with an electrical discharge nozzle. The spectral analysis revealed the formation of cyanopolyynes (HC_nN) with n up to 11, molecular species known to be present in the interstellar medium. Since acetonitrile itself is also a source of these linear chains under electrical discharge conditions, it was of interest to find out whether and if so, to what extent, phenanthrene also participates in the formation of these linear chains. In a further electrical discharge experiment with phenanthrene in mixture with $^{13}C_2$-acetonitrile, the species $HC_4{}^{13}CN$ could be observed, thereby confirming the contribution of phenanthrene to the formation of the cyanopolyynes.

High Resolution Infrared Spectroscopy of Aziridine-2-Carbonitrile

K. Keppler[1], S. Albert[1], C. Manca Tanner[1], J. Stohner[2], M. Quack[1]*

[1]ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland, [2]ZHAW, ICBT Institut für Chemie und Biotechnologie, 8820 Wädenswil, Switzerland

Molecular parity violation has been critically discussed in relation to homochirality and early biochemical evolution [1]. In this context molecules of potential importance for prebiotic chemistry are of interest [2]. The small chiral three-membered heterocyclic molecule aziridine-2-carbonitrile (2-cyano-aziridine) has been previously examined in [3] and the parity violating energy difference between the enantiomers in their ground state has been calculated [4]. Molecular parameters for the ground state of this molecule are available from earlier microwave studies [5], and its conformations have been examined by ab initio theory [6]. Here we report initial results of a high resolution spectroscopic study of cyano-aziridine. The spectrum has been measured at room temperature using the Bruker IFS125 Zurich Prototype (ZP2001) Fourier transform spectrometer [7,8] with a resolution of 0.0011 cm^{-1}. Transitions associated with the ν_{15} and ν_{16} bands in the 800−1000 cm^{-1} region have been assigned, and molecular parameters have been determined using the Watson Hamiltonian. Simulations performed using these parameters reproduce the observed spectra well. The results are discussed in relation to astrophysical spectroscopy and recent efforts on parity violation in chiral molecules [9].

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High Resolution Infrared and Terahertz Spectroscopy of Cyano-oxirane

K. Keppler[1], S. Albert[1], Z. Chen[2], P. Lerch[3], C. Manca Tanner[1], J. Stohner[4], M. Quack[1]*

[1]ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland, [2]Lanzhou University, College of Chemistry and Chemical Engineering, 730000 Lanzhou, Gansu, China, [3]Swiss Light Source, Paul Scherrer Institute, 5232 Villigen, Switzerland, [4] ZHAW, ICBT Institut für Chemie und Biotechnologie, 8820 Wädenswil, Switzerland

Oxiranecarbonitrile (cyano-oxirane) is of interest as a possible chiral precursor molecule of evolution [1]. In view of possible experiments and biomolecular homochirality, we have previously calculated parity violation in this molecule [2]. The spectrum of the molecule has previously been investigated in the microwave, millimeter, submillimeter [3] and terahertz [4] regions. We have recorded its infrared spectrum at 295K with a resolution of 0.0011 cm^{-1} using the Zurich Prototype ZP 2001 FTIR Spectrometer [5] and have conducted a rovibrational analysis of two thousand transitions associated with the ν_{12} (915.3 cm^{-1}) and ν_{13} (848.2 cm^{-1}) fundamentals using a Watson Hamiltonian and the WANG program [6]. This analysis, which included not only newly assigned infrared transitions but also molecular parameters and ground state energies obtained from our work in the THz region [4], has resulted in accurate molecular parameters for cyano-oxirane. Simulations performed using the parameters reproduce the observed spectrum well. Our results will be discussed as they pertain to astrophysical spectroscopic searches and the evolution of biomolecular homochirality [7].

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A Quantum Cascade Laser compact scheme for Carbonyl Sulfide detection for environmental monitoring

D. K. Pallotti[1], L. Santamaria Amato[1], M. Siciliani de Cumis[1], S. Viciani[2], M. Barrucci[2], A. Montori[2], F. D'Amato[2]

[1]Agenzia Spaziale Italiana, [2]Istituto Nazionale di Ottica

Carbonyl sulfide (OCS) is one of the gas in the Earth's atmosphere containing sulfur. It is involved in the global sulfur cycle, in particular in tropospheric and stratospheric regions. OCS also has an important role for biological applications. OCS natural emissions occur from volcanos, hot springs, and oceans. In addition, it could be produced in forest or biomass burning.

Here we present a project of portable, compact instrument for OCS detection. It will be based on the well known technique of tunable laser absorbtion spectroscopy TLAS.

The basic of TLAS technique is simple. The laser wavelenght is tuned over a particular absorption line of the analyte and the intensity of the transmitted radiation is measured. This intensity is related to the concentration of the gas by the Beer-Lambert law. The architecture of such device is based on a low consumption Quantum Cascade Laser around 5 microns provided by Alpes lasers. Due to natural lower OCS concentration, a 76-m multipass cell (Aerodyne Research) it is necessary to enhance the optical path for light interaction with the gas. The electronic to control the instrument and for signal acquisition will be based on compact Field Programmable Gate Arrays.

Analysis of high-resolution FTIR spectra of tritiated water vapour (HTO, DTO, and T_2O)

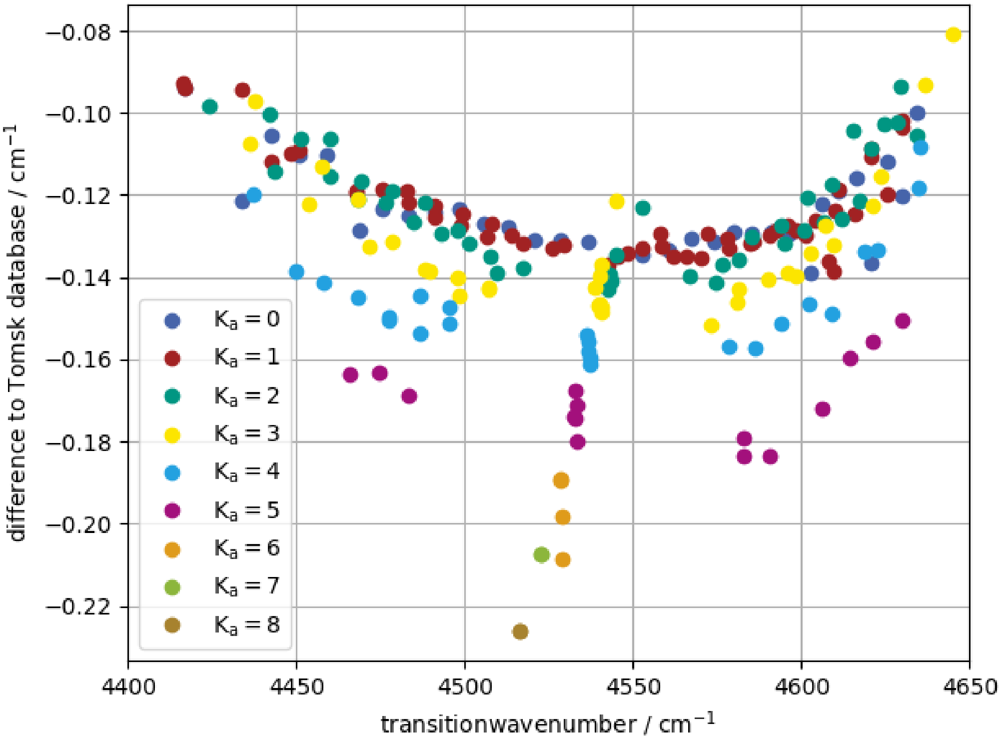
V. Hermann[1], P. Lingnau[1], M. Kamrad[1], M. Gaisdörfer[1], J. Reinking[1], M. Schlösser[1], F. Hase[2], J. Orphal[2]

[1]KIT IAP-TLK, [2]KIT IMK-ASF

High-resolution infrared spectra of tritiated water vapour ($HT^{16}O$, $DT^{16}O$, and $T_2{}^{16}O$) are sparse, but of great interest for the validation and improvement of ab-initio and variational calculations [1], for process monitoring in thermonuclear fusion reactors[2], and as input for theoretical calculations of fusion fuel cycles and their optimization. In a previous HRMS conference, we presented a novel spectroscopy cell for high-resolution FTIR spectrometry of the tritiated water isotopologues [3].

High resolution spectra of a tritiated vapour sample (A<1 GBq) by a BRUKER IFS 125HR with a resolution of 0.0075 cm^{-1} and an accuracy of the line positions of up to 10^{-4} cm^{-1}. The lines were assigned with the help of variational line lists from the Tomsk database[4]. Six bands of HTO, one of DTO and one of T_2O have been analysed in the spectral range from 2450 cm^{-1} to 6450 cm^{-1} with a total of more than 2000 lines. The observed differences between the measured line positions and the theoretical predictions are of the order of 0.1 cm^{-1}. Furthermore, a shift within a band correlated to the quantum number K_a is observed.

The detailed analysis will be demonstrated for the $T_2{}^{16}O$ (101) band and a comparison between measurement and predictions from theory will be made. Concerning the relative line intensities, very good agreement is observed.



Difference of the observed line positions to the variational calculations for different K_a

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QCL spectroscopy of SO_2 lines diluted in CO_2 and N_2 in view to planetological applications - preliminary results

B. Vispoel[1,2], L. Fabris[1], T. Roland[1], M. Appart[1], O. Browet[1], S. Robert[2,3], A. Vandaele[2], M. Lepère[1]*

[1]Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, 61, Rue de Bruxelles, Namur, Belgium, [2]Royal Belgian Institute for Space Aeronomy (BIRA-IASB), 3 Avenue Circulaire, Brussels, Belgium, [3]Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Chemin du Cyclotron 2, 1348 Louvain-la-Neuve, Belgium

With similar size but CO_2-rich atmosphere with sulfuric acid clouds, extreme temperature and pressure conditions at its surface, Venus is often described as the nightmarish little sister of Earth. The *VenSpec-H* instrument, developed by BIRA-IASB, and very recently selected by ESA [1], will be launched in 2031-2032 and will observe the atmosphere of Venus in the infrared to measure the abundances of trace gases like water vapor, carbon monoxide or sulphur dioxide, which could be related to volcanism or to other surface processes. For the inversion of atmospheric spectra obtained by *VenSpec-H,* the knowledge of absorption line parameters of these molecules will be required.

In this context, we have just started a spectroscopic study of sulfur dioxide. The preliminary work is devoted to the study of the collisional broadening coefficients of one line in the ν_3 vibrational band of SO_2 diluted in carbon dioxide (CO_2) and nitrogen (N_2). The measurements were performed using a quantum cascade laser spectrometer (QCL) that we have developed very recently. This dual beam spectrometer has both a very high spectral resolution (~10^{-4} cm^{-1}) and an excellent signal to noise ratio (~2000). Measurements were carried out at room temperature and for different pressures comprised between 5 and 50 mbar. The collisional half-widths at half maximum (HWHM) were deduced from individual fits on the experimental line shape, considering the Voigt, the Rautian-Solbel'Man and the Galatry models. Our results are compared with the literature. This preliminary study has to be continued for different lines at various temperatures, and considering the temperature dependence law [2]. The measurements will be realized by QCL spectroscopy and by Dual-Comb Spectroscopy, allowing to record spectra on a large spectral range [3].

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Validation tests of the W2020 energy levels of water vapor

A. Campargue[1], S. Mikhailenko[2,4], S. Kassi[1], A. Koroleva[3,1], S. Vasilchenko[2]

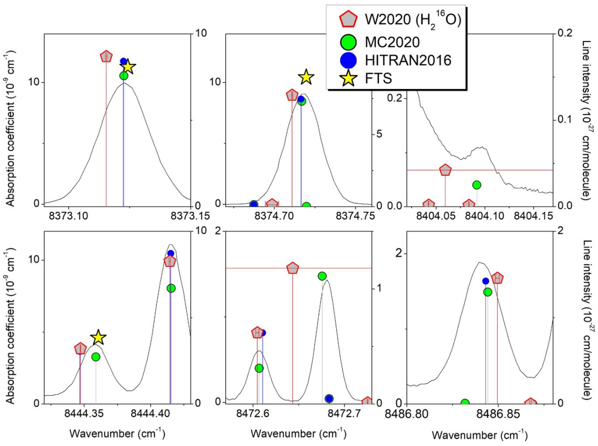
[1]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, [2]V.E. Zuev Institute of Atmospheric Optics, SB, Russia, [3]Institute of Applied Physics of RAS, Nizhniy Novgorod, Russia, [4]Climate and Environmental Physics Laboratory, Ural

A decade ago, a task group (TG) of the International Union of Pure and Applied Chemistry (IUPAC) performed an exhaustive collection and review of measured transitions, applied the MARVEL procedure and derived recommended empirical energy levels for nine major water isotopologues. Very recently, using an improved methodology, the sets of empirical energy levels of $H_2{}^{16}O$, $H_2{}^{18}O$ and $H_2{}^{17}O$ were updated leading to the so-called W2020 energy levels and transition wavenumbers [Furtenbacher et al. J. Phys. Chem. Ref. Data 49 (2020) 043103; https://doi.org/10.1063/5.0030680].

Here we present validation tests of the W2020 line list of $H_2{}^{16}O$ against spectra recorded by cavity ring down spectroscopy (CRDS) referenced to a frequency comb (FC), newly recorded in the 8040-8630 cm^{-1} region. The recorded spectra are found in excellent agreement with previous high quality studies available in the literature. While these literature sources were all incorporated in the transition database used to derive the W2020 energy levels, the direct superposition the FC-CRDS spectra to the W2020 line list of $H_2{}^{16}O$ shows a number of large disagreements. Deviations largely exceeding the W2020 claimed uncertainty on the transition frequencies are noted. The resulting W2020 list is thus less accurate that some of the published original sources used to derive the W2020 energy levels. We conclude that the sophisticated global procedure and algorithm elaborated to identify and weight adequately inaccurate line positions among the large W2020 transition database do not prevent less accurate data to spoil higher quality data sources.

The W2020 list of $H_2{}^{16}O$ is also compared to newly recorded CRDS spectra in the 13000-13200 cm^{-1} region (corresponding to the region of the A-band of O_2) where previous observations were very scarce. In the same way than in the previous region, important position deviations are evidenced and the W2020 error bars are found to be strongly underestimated.

SNM activity was also partly supported in the frame of the Russian Science Foundation, grant no. 18-11-00024-П. CRDS measurements near 760 nm were performed at IAO-Tomsk and funded by RFBR project 20-32-70054.



Modeling MW opacities of NH_3, SO_2 and PH_3 for planetary environments using HITRAN

F. S. Skinner[1], R. J. Hargreaves[1], I. E. Gordon[1]

[1]Harvard-Smithsonian Center for Astrophysics

The HITRAN (high-resolution transmission) molecular spectroscopic database is an international standard for reference molecular spectroscopy, particularly in simulating planetary and terrestrial atmospheric spectra [1]. Recently, new H_2-, He-, CO_2- [2, 3] and H_2O-broadening [4] parameters, which are relevant to planetary and exoplanetary atmospheres, have been added to HITRAN for many chemical species. Proof-of-concept comparisons for NH_3 have been performed against opacity models and laboratory data utilized by the Juno Mission, using the HITRAN Application Programming Interface (HAPI) [5]. The microwave radiometer on Juno is probing the atmospheric composition of Jupiter in the microwave range (0.02-0.73 cm^{-1}) [6, 7]. At these frequencies, Jupiter's atmospheric spectra is dominated by the inversion of NH_3 and is broadened by H_2, He, and H_2O. Additionally, due to the recent tentative detections of PH_3 on Venus [8], and the potential of spectral blending between transitions of PH_3 and SO_2, we have compared SO_2 and PH_3 absorption in the microwave region to experimental observations. The results of this work demonstrate that HAPI can be used with HITRAN data to produce atmospheric opacities under Jovian conditions in the microwave region.

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Spectral purity transfer to the UV region for spectroscopy based primary thermometry

A. Sorgi[1,4], C. Clivati[2], F. Levi[2], S. Gravina[3], L. Gianfrani[3], P. Cancio Pastor[1,4]*

[1]INO, Istituto Nazionale di Ottica-CNR, Largo E. Fermi 6, Florence I-50125, Italy, [2]INRIM, Istituto Nazionale di Ricerca Metrologica, Torino, Italy, [3]Dipartimento di Matematica e Fisica, Universitá della Campania , [4]LENS, European Laboratory for Nonlinear Spectroscopy, Via N. Carrara 1, Sesto Fiorentino I-50019

High precision laser spectroscopy of atomic or molecular gases has become a fundamental tool in experimental physics with applications ranging from determination of fundamental constants and frequency metrology to environmental science. Doppler-Broadened Thermometry (DBT) has been demonstrated to be a powerful technique for the precise determination of the Boltzmann constant, k_B [1,2], and accurate primary thermometry [3,4]. In particular, the variety of favorable features of Hg atom for Doppler Broadened DBT, when applied to the UV transition at 253.7 nm, makes Hg based DBT an excellent candidate as optical primary thermometry technique, hence contributing to the dissemination of the new kelvin, according to the 2019-redefinition. DBT is based on the precise measurement of the Doppler contribution to the spectral linewidth of the targeted transition. The requirement for attaining the goal uncertainty (1 ppm) on the Doppler width of the 253.7 nm Hg transition, hence to have a relative uncertainty on the temperature measurement of about 2 ppm, is to probe the absorption line with an ultra-narrow UV laser source (about 1 kHz) whose frequency is precisely tuned across 6 GHz frequency for a linear scan of the Doppler-broadened lineshape. The coherent UV radiation with such precision and stability is provided by frequency quadruplication of an extended cavity diode laser (ECDL) at 1014.8 nm [5].

Here, we present the adopted scheme for spectral purity transfer and frequency control of our ECDL in a Slave-Master configuration [6], where the Master Laser (ML) is an ultra-narrow linewidth single mode continuous wave laser at 1540 nm and the Slave Laser (SL) is the ECDL at 1014.8 nm. Direct Digital Synthesis (DDS) scheme uses an Optical Frequency Comb (OFC) as a bridge between ML and SL frequencies. The OFC offset-free beatnote of ML with the nearest OFC tooth is the DDS clock oscillator. Taking into account the NM and NS OFC-orders at the ML and SL frequencies, the DDS synthesized frequency (i.e DDS clock multiplied by a factor NM/NS), is used as the local oscillator in a Phase-Lock Loop (PLL) to phase-lock the SL to ML. Long term frequency control of the ML against the OFC using a second PLL circuit, guarantees primary frequency traceability of the SL. A 1-s stability of or and absolute accuracy of or for the generated UV frequency is expected, depending if the OFC is disciplined against to Quartz-Rb-GPS oscillator or to a fiber-disseminated optical frequency reference, respectively. SL frequency noise have been characterized.

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Low cost lock-in amplifier for absorption spectroscopy

D. K. Pallotti[1], M. Barbieri[2], L. Santamaria Amato[1], M. Siciliani de Cumis[1]

[1]Agenzia Spaziale Italiana, [2]University Medicine Göttingen

In Lock-In Amplifier (LIA) is an extremely versatile instrument widely used in several scientific and research fields like optics and photonics, material science, nanotechnology and sensing. In particular, found applications whenever we need to measure a very low AC signal with known frequency disturbed or enclosed in a background noise. LIA can detect inputs up to few nanovolts, where the signal to noise ratio represents one of the bigger bottlenecks. One of the drawbacks is surely represented by the cost: hardware configuration, processors and general characteristics in commercial LIA offer high performance at the expense of portability and price, especially with respect to the final goal in the typical applications.

A solution is offered by modern digital microprocessors, controllers or integrated boards that allow obtaining a digital LIA with customized characteristics, portable, low cost and possibly totally embedded in an experimental setup. For example, using a reprogrammable hardware circuit like a FPGA for the implementation of a LIA can bring several advantages. Moreover, the increased combining the hardware with a LabVIEW-based software, obtaining a higher customization level. In this work, we explore the possibility of developing a LIA by the use of LabVIEW facilities for acquiring and manipulating data collected thought the Red Pitaya STEMlab 125-10 board. We compare the general performances of the instrument with the one of commercial digital lock-in, the HF2LI from Zurich Instruments. Our LIA will be possibly used for absorption spectroscopy testing and measurements and in embedded stand-alone systems.

Total Internal Partition Sums for the HITRAN2020 database: TIPS_2021_v1p0.for and TIPS_2021_v1p0.py

R. R. Gamache[9], B. Vispoel[2,8], M. Rey[3], A. V. Nikitin[4,5], V. G. Tyuterev[5,3], O. Egorov[5,4], I. E. Gordon[6], V. Boudon[7]

[1]EEAS, University of Massachusetts Lowell, [2]BIRA-IASB, [3]Groupe de Spectrométrie Moléculaire et Atmosphériq, [4]Laboratory of Theoretical Spectroscopy, V.E. Zuev , [5]Laboratory of Quantum Mechanics of Molecules and R, [6]Harvard-Smithsonian Center for Astrophysics, [7]Laboratoire Interdisciplinaire Carnot de Bourgogne, [8]Research Unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur , [9]Department of Environmental, Earth, and Atmospheri

Total internal partition sums (TIPS) are reported for the 181 isotopologues of 57 molecules important in planetary atmospheres. Molecules 1 to 55, with the exception of #34 atomic oxygen, are taken from the HITRAN2020 list, and for some molecules additional isotopologues are considered. Molecules 56 and 57 are C_3H_4, CH_3, respectively. New to TIPS are the calculations for $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$, $^{14}N^{16}O$, $^{15}N^{16}O$, $^{14}N^{18}O$, $^{16}O^{32}S^{18}O$, $^{33}S^{16}O_2$, $^{15}N^{16}O_2$, ^{18}OH, ^{16}OD, $^{35}Cl^{16}O$, $^{37}Cl^{16}O$, $^{16}O^{13}C^{34}S$, $^{32}S^{19}F_6$, $^{12}C_2H_5D$, $^{12}C_2H_3D$, $^{12}C^{19}F_4$, $^{12}CH_3{}^{19}F$, $^{70}GeH_4$, $^{72}GeH_4$, $^{73}GeH_4$, $^{74}GeH_4$, $^{76}GeH_4$, $^{12}CH_3{}^{127}I$, $^{13}CH_3{}^{127}I$, and $^{14}N^{19}F_3$. In addition, all the molecules/isotopologues that were not recalculated for TIPS2017 (Gamache *et al.*, JQSRT 203, 70, 2017) have been recalculated using the 2014 CODATA physical constants and in some cases (e.g. O_3, CS_2, ...) updated spectroscopic information

The TIPS are determined by various methods generally from 1 to 5000 K. The details of these calculations are presented in Ref [1]. Recall of these data can be done with new versions of the TIPS codes: TIPS_2021_v1p0.for and TIPS_2021_v1p0.py.

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MCRB line shape parameters for the H_2O-N_2, H_2O-O_2, and H_2O-air collision systems for the HITRAN and GEISA databases

R. R. Gamache[1], B. Vispoel[2,3]

[1]Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, [2]BIRA-IASB, [3]Research Unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur

Modified Complex-Robert-Bonamy calculations [1,2] of the half-width, γ, and line shift, δ, were made for the $H_2{}^{16}O$-N_2, $H_2{}^{16}O$-O_2 collision systems. The calculations were done for all unique rotational transition quantum numbers for the rotation band and for 0-4 vibrational quanta exchanged in the ν_1, ν_2, and ν_3 bands for 13 temperatures from 200-3000 K.

First, the intermolecular potentials for the H_2O-N_2, H_2O-O_2 collision systems were adjusted to agree with trusted measurement values. Then, the MCRB calculations were made for 94,536 ro-vibrational transitions. These calculations give γ and δ for the transitions described above at the 13 temperatures of the study. These data were used to determine line shape parameters (LSP) for the H_2O-air collision system at the 13 temperatures of the study. The temperature dependence of γ and δ were determined via the Gamache-Vispoel model [3]; the temperature dependence of γ was also determined using the power law model. These data were then used to develop an algorithm that can predict the LSP with a standard deviation of ~5% for γ and average deviation of better than 0.002 cm^{-1} atm^{-1} for δ [4]. This procedure was applied at each temperature of the study, which allows the prediction of the T-dependence for H_2O-air.

The MCRB calculated line shape parameters and the prediction routine data were made part of an algorithm to add air-broadening line shape information to the databases. The algorithm is rather complicated by the fact that the data availability varies greatly with isotopologue. The table below shows the number of line shape data for $H_2{}^{16}O$ added to HITRAN and to GEISA from the various sources. The MCRB and prediction data provide far more data than the other sources.

	γ(H_2O-air)	δ(H_2O-air)	DPL(γ)	DPL(δ)	PL(γ)	PL(δ)
Priority data	4 660	3 582			4 340	
Intercomparison data	2 625	700			250	
Single measured datum	5 403	3 270			33	
MCRB data	24 503	25 737	29 236	29 255	26 208	25 315
Predicted data	129 317	133 167	136 954	136 932	135 625	122 358

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Improving the rotation vibrational line lists for ozone

A. Upadhyay[1], O. L. Polyansky[1,2], A. Owens[1], N. F. Zobov[2], E. K. Conway[3], J. Tennyson[1]*

[1] UCL Department of Physics and Astronomy, [2]Institute of Applied Physics, Russian Academy of S,
[3]Atomic and Molecular Physics , Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA

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There are long running problems over the precise transition intensities and line positions for ozone [1,2]. In our work, state of the art, first principles quantum mechanical methods are being used to compute high accuracy transition intensities and line positions for the microwave and infrared regions of the spectrum of ozone. In this poster I will discuss details of our most recent calculations of the ab initio dipole moment surface (DMS) and analysis of experimental ozone line positions using the MARVEL (Measured Active Rotation Vibration Energy Levels) technique [3]. To improve the quality of our current [4] DMS we are exploring the electronic structure model, finer grids and larger basis set sizes. The ozone MARVEL project currently involves the analysis of around 70 sources of scientific literature (we anticipate this number to increase). We will use the MARVEL energy levels to fit a new potential energy surface for ozone. We also intend to replace the calculated energy levels with MARVEL energy levels in our line lists. We hope the results of this study will be important for a range of atmospheric studies, such as self-consistency of ozone concentration retrievals in remote sensing techniques, and possible detections of ozone in exo-planetary atmospheres.

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An ExoMol line list for SO: Rovibronic spectrum of Sulfur Monoxide

R. Brady[1], G. Kim[2], W. Somogyi[3], J. Tennyson[3], S. N. Yurchenko [3]

[1]Department of Physics and Astronomy , London, UK, [2]Dharma College, Seoul, Korea, [3]Department of Physics and Astronomy, London, UK

The work we present here is a diatomic molecule line list study on the molecule Sulfur Monoxide (SO), suitable for characterising exoplanetary atmospheres up to temperatures of 4000 K. The motivation of this project is to provide comprehensive line list data applicable to modelling high temperature spectra in environments such as e.g. exoplanetary atmospheres, where current spectroscopic databases provide only limited coverage. The new SO line list will be included into the ExoMol database [1]. A production of such a line list first includes the creation of a MARVEL [2] set of rovibronic energies, calculation of high-level *ab initio* potential energy curves (PECs), spin-orbit curves (SOCs), electronic-angular momentum curves (EAMCs) and transition moment dipole curves (TDMCs) using MOLPRO at MRCI level of theory and a solution of coupled rovibronic Schrödinger equations using the variational code Duo [3]. The PECs, SOCs and EAMCs of Sulfur Monoxide were represented by analytical parametrised functional forms and refined by fitting to the MARVEL energies. A rovibronic line list for SO consists of energies, frequencies, Einstein coefficients and a partition function covering all electronic states up to 50 000 cm^{-1}, including X $^3\Sigma^-$, A $^3\Pi$, A′ $^3\Delta$, A" $^3\Sigma^+$, B $^3\Sigma^-$, C $^3\Pi$, a $^1\Delta$, b $^1\Sigma^+$ and c $^1\Sigma^-$. IR/Vis/UV absorption and emission spectra of SO for a set of temperatures are generated using the program ExoCross [4].

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Cold spectra of CF_4 analysis in the range 2160 – 2210 cm^{-1}

I. S. Chizhmakova[1,5], M. Rey[2], A. V. Nikitin[3], V. G. Tyuterev[1,2], L. N. Sinitsa[4], V. I. Serdyukov[4], A. A. Lugovskoi[4]

[1]Laboratory of Quantum Mechanics of Molecules and Radiative Processes, NR TSU, 36 Lenin Avenue, 634050 Tomsk, Russia, [2]GSMA, UMR CNRS 7331, Université de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France, [3]Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russia, [4]Laboratory of Molecular Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russia, [5]Institute of Monitoring of Climatic and Ecological Systems, Russian Academy of Sciences, 10/3, Academichesky Avenue, 634055 Tomsk, Russia

Information on the ro-vibrational high-resolution spectra of molecules is necessary for solving numerous problems associated with the study of the Earth's atmosphere. The CF_4 molecule though being yet minor impurities, have a particularly long the Earth's atmospheric lifetime and their very big estimated global warming potentials are expected to rapidly increase in the future [1]. Its feature is a presence of relatively low vibrational frequencies that makes the Boltzmann population of the excited levels important. Calculation of the spectra of polyatomic molecules is a difficult task, due to the large dimension and the need to perform high-precision ab initio calculations [2].

The spectra of CF_4 have been measured on Fourier transform spectrometer Bruker IFS-125M by using a single-pass low-temperature cell 220 cm long at temperatures between 205 and 300 K [3]. The spectrum modelling was performed thanks to MIRS software [4] based on tetrahedral tensorial formalism [5]. By combining non-empirical contact transformation Hamiltonians fitted to observed values for line positions and ab initio based variational calculation for line intensities, we obtained correct spectra simulation of several cold and hot bands of CF_4 in the region. In this work we report the analysis of rovibrational interacting bands of CF_4 molecule [6], for reliable simulation atmospheric absorption of this molecule in the region between 2160 – 2210 cm^{-1}, including the most significant hot bands.

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Towards a complete elucidation of the ro-vibrational band structures in the SF_6 infrared spectrum from full quantum-mechanical calculations

M. Rey[1], I. S. Chizhmakova[2], A. V. Nikitin[3,2], V. G. Tyuterev[2,1]

[1]Groupe de Spectrométrie Moléculaire et Atmosphériq, [2]Laboratory of Quantum Mechanics of Molecules and R, [3]Laboratory of Theoretical Spectroscopy, V.E. Zuev

SF_6 is an important greenhouse molecule with a very long lifetime in the atmosphere and because of its relatively low vibrational frequencies, the hot bands contribute significantly to the absorption infrared spectra, even at room temperature. The calculation of complete rovibrational line lists required for a fully converged opacity modeling is thus extremely demanding, making the use of specific tools (symmetry, compression, reduction) mandatory to reduce the computational costs.

In this work, first accurate and complete theoretical room-temperature rotationally-resolved spectra in the range 300-3000 cm^{-1} are reported for the three most abundant isotopologues ($^{32}SF_6$, $^{33}SF_6$ and $^{34}SF_6$) [1]. More than 2600 new vibrational band centers were predicted using our empirically-refined *ab initio* potential energy surface [2] and highly-excited rotational states were calculated up to $J = 121$. This results in 6 billion transitions [1] computed from an *ab initio* dipole moment surface [2] and distributed over more than 500 cold and hot bands. For the first time, the major (ro)vibrational band structures in the wavenumber range corresponding to the strongest absorption in the infra-red are completely elucidated for a seven-atomic molecule and are in excellent agreement with observed PNNL spectral patterns [3].

For applications requiring accurate opacity calculations with a temperature dependence, our complete theoretical line lists should thus be preferred to partial lists included in all other available databases. The final line lists are made available through the TheoReTS [4] information system (http://theorets.univ-reims.fr, http://theorets.tsu.ru).

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Binary absorption continua of CO_2-H_2O mixtures for planetary applications.

H. Fleurbaey[1], D. Mondelain[1], R. Grilli[2], Y. Carreira Mendes da Silva[1], S. Kassi[1], A. Campargue[1]

[1]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, [2]Univ. Grenoble Alpes, CNRS, IGE, 38000 Grenoble

Accurate modeling of the absorption of CO_2-rich gas mixtures is of great importance for planetary sciences.

In particular, a better understanding of the continua of CO_2-H_2O and CO_2-H_2 mixtures will impact the modeling of early Mars climate. The CO_2-H_2O binary continuum is also crucial to study the evolution of rocky planets in the early "magma-ocean" stage.

To this purpose, we used high-sensitivity cavity enhanced absorption techniques (CRDS and OF-CEAS) to record spectra of CO_2-H_2O mixtures in several spectral regions corresponding to transparency windows of CO_2 and H_2O where the monomer absorption is weaker: 1.5-1.53 µm, 1.68-1.75 µm, 2.06 µm, 2.2-2.35 µm and 3.5 µm.

We then subtracted the various contributions to the observed absorption (monomer absorption and self-continua of both CO_2 and H_2O) to reach the binary continuum absorption which is proportionnal to the product of the densities of the two mixed species.

Experimental room temperature binary coefficients are compared to the only available models based on line shape profiles with chi-factors.

New line list of $^{12}CH_4$ in the range 4100-4300 cm^{-1}

A. A. Rodina[1], X. Thomas[2], L. Daumont[2], L. Manceron[3,6], A. Protasevich[1], K. Sung[4], V. G. Tyuterev[5,2], A. V. Nikitin[1]*, M. Rey[2]*

[1]V.E. Zuev Institute of Atmospheric Optics SB RAS, Akademician Zuev Sq 1., Tomsk, 634055 Russia, [2]Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France, [3]AILES Beamline, Synchrotron SOLEIL, L'Orme des Merisiers St-Aubin BP48, F-91192 Gif-sur-Yvette Cedex France, [4]Jet Propulsion Laboratory, California Institute of Technology 4800 Oak Grove Drive, Pasadena, CA 91109, USA, [5]QUAMER laboratory, Tomsk State University 36, Lenin Ave., Tomsk, 634050 Russia, [6]Sorbonne Université, CNRS, MONARIS, UMR 8233 4 place Jussieu, Paris, France

Over the past decades, improving knowledge of the infrared spectra of methane has become the goal of numerous atmospheric and astrophysical applications [1–2]. In this context, many studies related to the radiative properties of the Earth's atmosphere have been published (see [3] for details and references). Another incentive is the study of the atmosphere of Titan (the largest satellite of Saturn), which consists of 98.6% nitrogen and 1.4% methane at temperatures from 70 to 200 K [4-5].

In this work, we study the spectra belonging to Octad (the third vibrational polyad). A new list of $^{12}CH_4$ lines in the 4100-4300 cm^{-1} range was obtained similarly to our recent work [3,6]. Four spectra of CH_4 in the 4100–4300 cm^{-1} region was recorded using Fourier transform spectrometer in Reims (France) with long optical paths (202 m, 602 m) at various pressures. Additional $^{12}CH_4$ spectra covering the same region were obtained at 80-123 K for various pressures and the path length of 93 m at the SOLEIL synchrotron setup in Paris; these spectra were used to identify the positions of the low *J* lines. In addition, the JPL spectra at 80 K for $^{12}CH_4$ [1] and $^{13}CH_4$ [7] were used to partially correct the positions and identifications for the low *J* lines. The positions and intensities of the observed transitions were obtained using nonlinear line profile fitting procedures. The assignment and analyses were carried out using effective Hamiltonian and effective dipole moment models. The reported list contains new positions and intensities for over 13000 lines including 2500 new lines corresponding to hot bands. In addition, the positions and intensities of $^{13}CH_4$ were improved using cold spectra. For the resulting list of lines, the positions and intensities are compared with the HITRAN 2016 database.

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High resolution infrared jet-cooled spectroscopy of furan compounds

P. ASSELIN[1], S. CHAWANANON[1]

[1]Laboratory MONARIS UMR 8233 CNRS, Sorbonne Université, Paris

style="text-align: justify;">Furan compounds are produced through hydrolysis-dehydration of cellulose and hemicellulose [1] and are largely used as intermediates to alkane fuels from biomass, industrial usages and biomass burning [2]. Among them, furfural (FF) can be transformed by hydrogenation in 2-methylfuran (2-MF) and both molecules are emitted into the atmosphere where their oxidation may lead to ozone and secondary organic aerosol formation [3]. Accurate spectroscopic data about such compounds become highly necessary to evaluate their fate and impact on air quality. In this context, high resolution infrared jet-cooled spectroscopy of FF and 2-MF were realized with an infrared quantum cascade laser (QCL) spectrometer coupled to a pulsed supersonic jet (SPIRALES setup) implemented at the MONARIS laboratory [4]. Three tunable QCLs were used to investigate the 980-1030 cm^{-1} and 1580-1720 cm^{-1} ranges. For both molecules, previous microwave studies enabled to characterize finely the ground state [5,6]. Quantum chemistry calculations provided good estimates of anharmonic frequencies and sets of excited state rotational constants to initiate rovibrational analyses. The present work reports the rovibrational analyses of three bands of furfural in the mid-infrared range according to the rigid rotor approximation : 2 fundamentals, ν_{14} (CH in plane bending) and v_5 (C=O stretch), and one intense combination band assigned to $\nu_{15}+\nu_{17}$. On the other hand, the more delicate analysis of both bands of 2-MF observed at 1015 and 1612 cm^{-1} which requires internal rotation treatment with a V_3 potential barrier (412.8 cm^{-1} in the ground state), is currently in progress.

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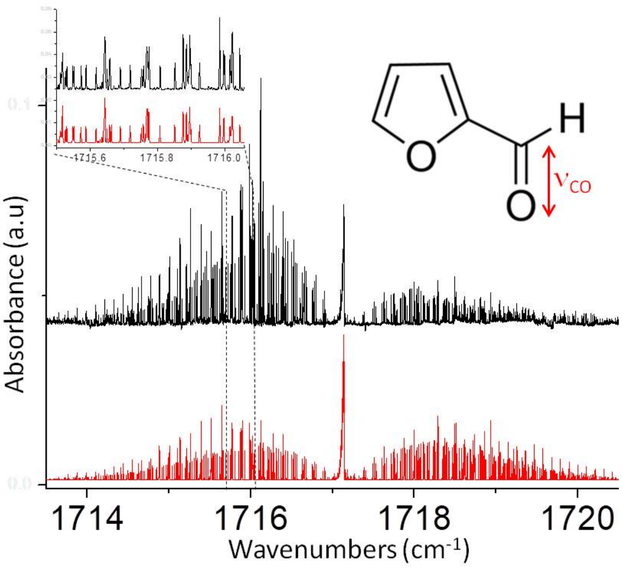


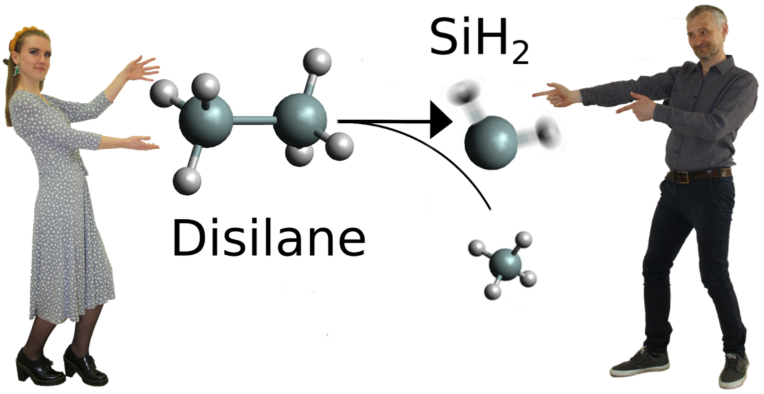
Jet-cooled laser spectrum of the CO stretching band of furfural compared to the simulated spectrum at a rotational temperature of 20 K.

Including Non-LTE Effects into ExoMol Line Lists

V. H. Clark[1], S. N. Yurchenko [1]*

[1]Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK

We have developed two new methodologies for the inclusion of non-LTE effects into the pre-existing line lists of the ExoMol Database (www.exomol.com) [1]. Two approaches for non-LTE vibrational populations of the product SiH_2 are introduced: a simplistic 1D approach based on the Harmonic approximation and a full 3D model incorporating accurate vibrational wavefunctions of SiH_2 computed variationally with the TROVE (Theoretical ROVibrational Energy) program [2,3]. The methodologies, named the 1D and 3D approach, work by calculating the integral of the overlap of wavefunctions between the molecules' ground and excited states. In this poster we'll describe both approaches using the SiH_2 system and our pre-existed SiH_2 line list, CATS [4]. We show how their non-LTE spectral signatures can be used to trace different reaction channels of molecular dissociations.



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Line shape parameter determination by quantum cascade laser dual-comb spectroscopy (DCS) – application to CH_4 diluted in N_2

M. Lepère[1], O. Browet[1], J. Clément[1], B. Vispoel[1,3], P. Allmendinger[2], J. Hayden[2], F. Eigenmann[2], A. Hugi[2], M. Mangold[2]

[1]Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, 61, Rue de Bruxelles, Namur, Belgium, [2]IRsweep AG, Laubisrütistrasse 44, 8712 Stäfa, Switzerland, [3]Royal Belgian Institute for Space Aeronomy (BIRA-IASB), 3 Avenue Circulaire, Brussels, Belgium

The IRis-F1 is a Dual Comb Spectrometer (DCS) built on quantum cascade laser frequency combs [1]. It allows to cover relatively large spectral ranges (~ 60 cm^{-1}) with high resolution (-1) in the mid-infrared region (1000-2500 cm^{-1}). In *rapid-sweep* technique [2], IRis-F1 records full spectra in only 6 ms, but the wavenumber information has to be inferred from the measurement. The *step-sweep* technique [3] guarantees an accurate knowledge of the relative frequency axis in a record time of several minutes. The two techniques will be detailed in [4].

Here, we present the in-depth characterization of the first-built *step-sweep* IRis-F1 which was recently delivered to Namur. We show that this type of DCS is very well adapted to the determination of line shape parameters, such as the collisional broadening. Next, we give the first results obtained in the ν_4 vibrational band of methane diluted in nitrogen at room temperature. After recording spectra, the collisional half-widths are deduced by fitting Voigt profile on experimental line shapes. Finally, our first results are compared with the literature.

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Measurements of intensities and self-broadening line shape parameters of H_2O absorption lines in the spectral range 700–2000 cm^{-1}

C. Röske[1], M. Birk[1], G. Wagner[1]

[1]German Aerospace Center (DLR)

A Bruker IFS 125HR Fourier transform interferometer in combination with a multireflection cell was used to measure pure water vapor transmission spectra in the range 700–2000 cm^{-1}. A total of 17 spectra with absorption path lengths between 14 m and 161 m and sample gas pressures from 0.01 to 20 mbar were measured at room temperature.

The recorded spectra were corrected for detector non-linearity, thermal self-radiation and for deviations from an ideal instrumental line shape. A multispectrum-fitting approach was used, applying a quadratic speed-dependent Voigt line model which was extended to account for Rosenkranz line mixing.

Experimentally determined line shape parameters are compared to the HITRAN database. Line intensities are also compared to values from two *ab initio* calculations [1][2]. The overall agreement with both is better than 0.5% for most lines.

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Laser ablation micro-laboratory for the generation of interstellar species

L. Kolesniková[1], I. León[2], E. R. Alonso[3,4], S. Mata[2], J. L. Alonso[2]*

[1]Department of Analytical Chemistry, University of Chemistry and Technology, Technická 5, Prague 6, 16628, Czech Republic, [2]Grupo de Espectroscopia Molecular (GEM), Edificio Quifima, Lab. de Espectroscopia y Bioespectroscopia, Parque Científico UVa, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, 47011, Spain, [3]Instituto Biofisika (UPV/EHU, CSIC), University of the Basque Country, Leioa, Spain, [4]Fundación Biofísica Bizkaia / Biofisika Bizkaia Fundazioa (FBB), Barrio Sarriena s/n, Leioa, Spain

The chemistry of the interstellar medium encompasses a large number of reactions acting on a plethora of species. The high amount of unstable species participating in these reactions drives an urgent need to develop efficient methods for the laboratory *in situ* generations of molecules with the aim to characterize them spectroscopically. Such laboratory experiments are crucial to decode the molecular universe by direct comparison of the interstellar and terrestrial spectra.

In the present contribution, we propose a new approach based on laser ablation of solid organic precursors. The chemical species generated in the throat of our laser ablation source are cooled in a supersonic expansion and monitored by high-resolution microwave spectroscopy. We experimentally demonstrate a simultaneous formation of an impressive number and variety of compounds including new chemical species of astrophysical interest using diaminomaleonitrile and uridine as prototypical precursors. With this "micro-laboratory" in hands, we extend the boundaries for the molecular *in situ* generations beyond traditional techniques such as electric discharge and pyrolysis.

An update for Methane line-mixing spectroscopic parameters and its importance for IASI retrievals

J. T. Erwin[1], B. Vispoel[1], A. C. Vandaele[1], C. Robert[1], M. De Mazière[1]

[1]BIRA-IASB

Line-mixing affects the methane absorption spectrum, and studies have suggested that it should be considered when deriving methane using remote sensing. The ‘1st order’ approximation of this process produces an additional line shape parameter to correct the computed absorption spectrum. The data necessary to compute these corrections is not contained in the standard HITRAN database. The most recent complete database was published to compute the 1st order correction for a selection of lines in the ν_3 and ν_4 band regions [1]. The HITRAN line-list has been significantly updated since that publication [2], and at this time a consistent and complete dataset is not available for line-mixing.

In this work, we include line-mixing for methane in the forward model of IASI spectra in the TIR [3], using the line-by-line retrieval software ASIMUT-ALVL [4]. We compare the effect of the model using spectroscopic parameters from three sources: a) Tran’s 2006 published values of line-mixing, b) HITRAN 2016 without line-mixing, and c) our effort to merge these two sources. Our effort includes updating the line-parameters from HITRAN 2016 for lines considered in [1] while retaining the same line-mixing parameters used to compute the 1st order correction, and to include other lines from HITRAN 2016 that were not considered in that work.

We found large differences in the absorption cross section between Tran 2006 and HITRAN 2016. In addition, we show that line mixing at Earth’s pressure and methane abundance has a small effect on the forward modelled irradiance. We will present results from a set of representative retrievals and highlight the significance of our three sources of spectroscopic parameters on the residuals.

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Rotational Spectrum of Methylamine in v_t=1 and v_t=2 Excited Torsional States

P. Gyawali[1], I. Kleiner[2], R. A. Motiyenko[1], I. Gulaczyk[3], M. Kręglewski[3], V. Ilyushin[4]

[1]Université de Lille, Laboratoire PhLAM, [2]Laboratoire Inter-universitaire des Systèmes Atmosphériques, CNRS, UMR7583, Université Paris Est-Créteil et Université de Paris, [3]Faculty of Chemistry, Adam Mickiewicz University, [4]Institute of Radio Astronomy of NASU

We present the assignment of the pure rotational transitions in v_t=1 and v_t=2 excited torsional states of methylamine. The assignments were made based on new measurements of the rotational spectrum of methylamine in the frequency range 150 to 1520 GHz using the Lille THz spectrometer. We used the predictions calculated using the hybrid program [1] that can fit rotational levels in molecules with one CH_3 internal-rotation large-amplitude motion, one NH_2 inversion large-amplitude motion. The dataset used to calculate the predictions already contains around 3000 MW and 26848 FIR transitions of v_t = 0, 1 and 2 of CH_3NH_2, which are fit to a weighted standard deviation of 1.75 using 102 parameters. In the THz spectra, the rotational transitions of v_t=1 state were easily located within few MHz vicinity of their predicted positions. The assignment of the rotational transitions in v_t=2 state was more complicated due to somewhat higher shifts between predicted and measured frequencies. In this case, to confirm the assignments we used Loomis-Wood type diagrams. In total, more than 2500 new rotational transitions of methylamine in v_t=1 and v_t=2 states were assigned and added to the existing dataset. The latest results of the global fitting of MW and FIR data will be presented.

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Singly deuterated Hydrogen Peroxide HOOD - The first torsional State

D. Herberth[1], T. F. Giesen[1], A. Körner[1]

[1]University of Kassel

We analysed the infrared spectrum of singly deuterated hydrogen peroxide HOOD up to 500 cm^{-1}, assigned 2440 ro-torsional transitions and derived accurate band origins and rotational constants for the first torsionally excited state n = 1. We observed numerous perturbations between nearby levels in n = 1, which were aggravating the assignment of transitions. Therefore, we performed an additional analysis with an automatic spectral assignment procedure algorithm (ASAP) and succeeded to determine the location of in total 588 ro-torsional energy levels in the first torsionally excited state and derived the K_a- and J-dependance of the torsional splitting.

New data for the ammonia spectra between 3900 and 4700 cm^{-1}.

P. Čermák[1], P. Cacciani[2], A. Campargue[3], J. Vander Auwera[4]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia, [2]Univ. Lille, CNRS, PhLAM, 59000 Lille, France, [3]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, [4]SQUARES, C.P. 160/09, Université Libre de Bruxelle

Room temperature absorption spectra of ammonia have been recorded by high-resolution Fourier transform spectroscopy in the range of 3900-4700 cm^{-1}. Positions and intensities of 8422 absorption lines were retrieved. Their intensities range between 3×10^{-25} to 1.6×10^{-20} cm/molecule. The rovibrational assignment was performed based on the C2018 theoretical line list [1] supported by the systematic use of Lower State Combination Difference (LSCD) relations. 5632 transitions were thus assigned to the main isotopologue, $^{14}NH_3$, and 620 transitions of the $^{15}NH_3$ isotopologue were identified. The achieved quality of the LSCD relations indicates that the precision of the reported line positions is better than 0.001 cm^{-1} for most of the lines. For a given transition, a comparison of the measured and calculated intensities with other transitions sharing the same upper state provided an additional helpful criterion. 2064 energy values of 29 upper vibrational levels are reported. The data represents a significant improvement compared to the HITRAN2020 database [2].

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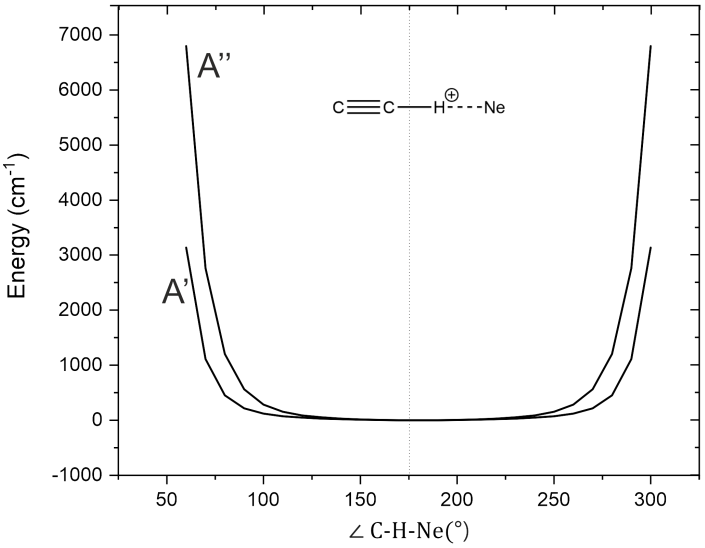
Elucidation of the Renner-Teller and spin-orbit splitting patterns in the IRPD spectra of C_2H^+

K. Steenbakkers[1], A. Marimuthu[1], L. Geessinck[2], F. Lipparini[3], J. Gauss[4], S. Schlemmer[5], J. F. Stanton[6], A. van der Avoird[7], G. C. Groenenboom[7], B. Redlich[1]*, S. Brünken[1]*

[1]FELIX Laboratory, Radboud University, [2]Theoretical Chemistry, Radboud University, [3]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, [4]Institut für Physikalische Chemie, Johannes Gutenberg Universität Mainz, [5]I. Physikalisches Institut, Universität zu Köln, [6]Department of Chemistry and Physics, University of Florida, [7]Theoretical Chemistry, Radboud University

Open-shell linear molecules, such as C_2H^+ in its $^3\Pi$ electronic ground state, are of basic spectroscopic interest due to their extremely complex vibrational spectra, which are a result of a combination of Renner-Teller and spin-orbit coupling [1]. The first broadband and narrow-linewidth vibrational IRPD (infra-red pre-dissociation) spectra of Ne- and He- tagged C_2H^+ ions have been obtained in the range 250-2000 cm^{-1} using the free electron laser FELIX interfaced with a cryogenic ion trap [2] and were analyzed with an effective Hamiltonian approach. These spectra reveal a clear picture of the Renner-Teller splitting patterns for both the He- and the Ne-tagged species and are clearly different from one another indicating a strong effect of the interaction with the rare-gas tag on the bending mode. Ab initio calculations show that the rare-gas atom attaches to the hydrogen with a shallow minimum at linear geometry, such that its vibrational modes strongly couple to the C-C-H bending. Figure 1 displays the calculated, extremely shallow potential of the C-H-Ne bending.



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Cavitiy-Enhanced and High Resolution Fourier-Transform Spectroscopy

A. Libert[1], B. Fabre[2], S. Robert[1], A. Roucou[1], X. Urbain[1], C. Lauzin[1]

[1]Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, [2]Université de Bordeaux-CNRS-CEA, CELIA, UMR5107, F33405 Talence, France

The perfect instrument in spectroscopy measures spectra with high-resolution, high-sensitivity and in a small amount of time over a broad spectral range. Fourier-transform spectrometers allow for both high resolution and broadband measurements thanks to their multiplex advantage. By coupling the light source to an optical cavity, the sensitivity of the instrument is considerably increased since the interaction length of the light with the sample is increased by several orders of magnitude (reaching kilometric interaction lengths). This poster presents the first results regarding the design and the fabrication of a homemade instrument that will embody all these features. This instrument is designed for the analysis of molecules in the gaseous phase from the near infrared to the UV ranges (2000-400 nm) with a resolution down to 0.0035 cm^{-1}. The spectrometer has the peculiarity to employ either a super-continuum laser or a femtosecond laser as the broadband light source. Cavity enhanced absorption spectrum of water from 10500 to 14300 cm^{-1} has been measured in order to evaluate the performances of the setup. These measurements were performed in an auto-balanced detection scheme with the supercontinuum laser. Finally, when performing spectroscopy of complex molecules in the gas phase at high resolution, spectra are highly congested because many energy levels are populated, allowing a great number of transitions to occur. This results in diffculties to assign each transition to its corresponding energy levels. One solution is to cool down the sample to a few Kelvin in order to populate only the first few energy levels. This cooling can be achieved either by buffer gas cooling or by the use of a supersonic jet. The design of the setup (under construction) to perform buffer gas cooling is presented as a short-term perspective.

The millimetre-wave spectrum of 2-hydroxyprop-2-en-1-al

J. Koucký[1], L. Kolesniková[1], K. Luková[1], P. Kania[1], Š. Urban[1]*

[1]University of Chemistry and Technology, Department of Analytical chemistry, Technická 5, 166 28 Prague 6, Czech Republic

style="text-align: justify;">Aldehydes belong to the group of molecules with recent interest for being discovered in the interstellar medium[1,2]. One of the possible interstellar candidates is 2-hydroxyprop-2-en-1-al, a dehydration product of glyceraldehyde and 1,3-dihydroxyacetone. Apart from its aldehyde functional group, it also contains a vinyl alcohol structural motif that has already been found in interstellar medium[3].

The high resolution rotational spectrum of 2-hydroxyprop-2-en-1-al was recorded with Prague millimetre-wave semiconductor spectrometer in two separate frequency regions (128–160 GHz and 285–329 GHz). With hundreds of rotational transitions we were able to determine up to sextic centrifugal distortion constants in the ground state. Together with the ground state, several series of low-lying vibrationally excited state were analysed with the help of theoretical predictions carried out with MP2 and DFT computational methods.

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Extending laboratory measurements of the CH_3O radical towards the terahertz domain

M. Martin-Drumel[1], O. Chitarra[1], J. Spaniol[1], J. Loison[2], T. Hearne[1], O. Pirali[1]*

[1]Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, France, [2]Université Bordeaux, CNRS, Institut des Sciences Moléculaires, France

Current astronomical observations, for instance with ALMA and NOEMA, extend well into the submillimeter-wave domain. For many molecules, including some that have already been detected in the interstellar medium, laboratory data remain limited to the microwave and millimeter-wave domain. This is particularly striking for reactive species that remain challenging to produce in the laboratory. Considering that frequency extrapolation in absence of laboratory data is particularly unreliable, this lack of measurements surely prevents some interstellar observations. The CH_3O radical is one such species: it is a known interstellar molecule [1] for which laboratory measurements do not extend beyond 370 GHz [2].

We have extended the measurements of the pure rotational spectrum of CH_3O towards the terahertz domain. The radical was produced by H-abstraction from methanol using atomic fluorine, itself produced using a microwave discharge in F_2 diluted in He, a method that we successfully used recently to investigate the rotation-tunnelling spectrum of the CH_2OH radical [3]. Compared to that previous work, several enhancements have been made to our (sub)millimeter-wave spectrometer that now allows for double-pass into the absorption cell and magnetic-field modulation. The strength of the double-modulation (source frequency and magnetic field) scheme is that only transitions of open-shell species are visible over a completely flat baseline, a feature that has proven invaluable in the case of CH_3O to disentangle an otherwise dense spectrum with numerous strong transitions arising from the precursor or other reaction products (such as H_2CO). Overall, about 500 lines of CH_3O have been recorded up to 900 GHz, with accuracies ranging from 10 to 200 kHz. These transitions have been fit, together with available pure rotation literature data, to a rigid-rotor Hamiltonian using the SPFIT/SPCAT software [4].

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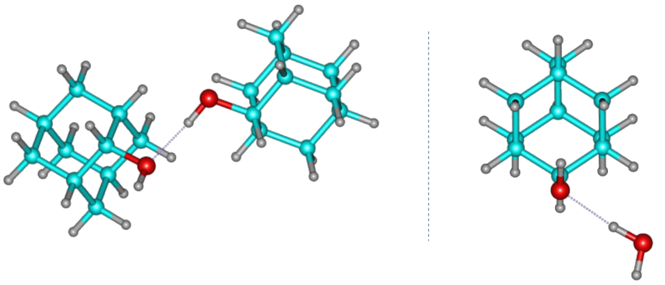
Hydrogen Bonding in the Dimer and Monohydrate of the Bulky Molecule of 2-Adamantanol Using Microwave Spectroscopy

A. Lesarri[1], M. Juanes[1], R. T. Saragi[1], L. Evangelisti[2], L. Enriquez[3], J. E. Rubio[3]

[1]University of Valladolid, Departamento de Química , [2]University of Bologna, Dipartimento di Chimica "G. Ciamician", [3]University of Valladolid, Departamento de Electrónica, ETSIT (Spain)

High resolution spectroscopic analysis on adamantane derivatives are interesting due to their structural similarity to the cubic crystal structure of diamonds. Here we present the conformational preferences of the 2-adamantanol monohydrate and the 2-adamantanol homodimer using chirped-pulse Fourier-transform microwave spectroscopy in a supersonic jet expansion. The analysis of the rotational spectrum, conducted in the region 2-8 GHz, shows that the alcohol group of adamantanol (left Figure) behaves as a proton acceptor and displays a moderate hydrogen bonding (r(O-H···O)~1.88Å) when combining with a molecule of water. Additionally, two homodimers (r(O-H···O)~1.90Å) have been characterized rotationally (right Figure), reducing the conformational complexity of cyclohexanol where six isomers were detected [1]. The relatively large molecular mass of the 2-adamantanol dimers (304 u) produces small rotational constants (B+C ~ 270 MHz), grouping the lines of the spectrum. The experimental work is supplemented with DFT and ab initio calculations.



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En route for the CH2OH radical interstellar detection: laboratory re-investigation of its rotation-tunneling spectrum

O. Chitarra[1], J. Spaniol[1], M. Martin-Drumel[1], B. Gans[1], J. Loison[2], L. H. Coudert[1], H. S. Müller[3], O. Pirali[1]*

[1]Institut des Sciences Moleculaires d'Orsay, [2]Institut des Sciences Moleculaires, [3]I. Physikalisches Institut, Universität zu Köln

Radical species are suspected to be involved in gas phase reactions occurring in the interstellar medium (ISM) and their detection gives important insights about the chemistry happening in the ISM. More specifically, methanol derivatives (CH_3O and CH_2OH) are considered key reactive intermediates in the formation of commonly observed complex organic molecules (COMs) [1]. Interestingly, despite the recent first laboratory detection of CH_2OH rotation-tunneling spectrum [2] and while this isomer is the most thermodynamically stable, only CH_3O has been detected in the ISM so far [3]. A plausible explanation to this lack of interstellar detection is the non-observation in the laboratory of the most intense transitions at low temperature.

We led a re-investigation in the submillimeter-wave region of the hydroxymethyl radical (CH_2OH) rotation-tunneling spectrum from 160 GHz up to 900 GHz. The radical was synthetized by H abstraction from methanol (CH_3OH) using F atoms produced by a MW discharge. CH_2OH pure rotational spectrum was recorded using a frequency multiplication chain spectrometer following a method described in ref. [4]. We further optimized the experimental set-up by multiplying the number of fluorine atoms injection (x3) to increase the concentration yield of the radical. We also doubled the path length using a roof top mirror and a polarization grid. Finally, we used a double modulation scheme for the detection: to the source frequency modulation, we added a magnetic field modulation to selectively detect transitions arising from open-shell species.

Our previous investigation [4] focused on transition up to 330 GHz. This present high-resolution study allowed the measurement of about 420 new lines up to 900 GHz. We were also able to measure, for the first time, the astrophysically relevant $1_{10}\leftarrow 1_{01}$ transition around 168 GHz. The interstellar search for the radical can now be undertaken in cold to warm environments of the ISM up to 900 GHz.

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Hyperfine structure in the microwave spectra of a few van der Waals complexes containing ammonia molecule

I. Tarabukin[1], L. Surin[1], A. van der Avoird[2]

[1]Institute of Spectroscopy, Russian Academy of Science, Troitsk, Moscow, Russia, [2]Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands

A nuclear hyperfine structure in molecular rotational spectra arises from magnetic and electric interactions of the molecular fields with the nuclear moments. Observation of the resulting splittings of the energy levels into components provides detailed information on the molecular electronic structure and chemical bonds. In the case of weakly bound molecular complexes, the hyperfine structure parameters (quadrupole coupling, spin-spin coupling, and spin-rotation constants) might provide additional valuable information about intermolecular dynamics and the interaction potential. In this work the results of hyperfine structure analysis of the recently observed spectra together with *ab initio* calculations of hyperfine structure parameters for the NH_3–Ne [1], NH_3/ND_3–H_2/D_2 [2] and NH_3–N_2 [3, 4] van der Waals complexes are presented.

The first detection of the missing (*para*)-NH_3–Ne nuclear spin isomer was performed at frequencies of 2-8 GHz [1] and the ^{14}N nuclear quadrupole coupling constant associated with the (*para*)-NH_3 subunit of the complex was precisely determined for the first time. In case of the deuterated NH_3–H_2 complexes the measured line positions (20-140 GHz) [2] included nuclear quadrupole splitting due to the ^{14}N nuclear spin of NH_3/ND_3 and the additional splitting due to nuclear quadrupole and spin-spin interactions of D nuclei of the D_2 unit. Very complicated hyperfine structure due to three ^{14}N nuclei was partly resolved and examined for the measured lines of the NH_3-N_2 complex in the frequency range of 6-26 GHz [3, 4]. For all studied complexes the determined experimental hyperfine structure parameters were compared with the theoretical values obtained from the expectation values $\langle P_2(\cos\theta_{NH3})\rangle$ over the *ab initio* bound state wave functions. The results provided the dynamical information about the angular orientation of ammonia (and hydrogen/nitrogen in appropriative case) units in the complexes, their structure and intermolecular dynamics.

The authors acknowledge the Deutsche Forschungsgemeinschaft (SCHN 1280/5), Russian Science Foundation (17-02-01395) and Russian Foundation for Basic Research (19-03-00998).

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Gas-phase IR spectra of two fundamental halocarbon cations: CH_2Cl^+, CH_3ClH^+

P. C. Schmid[1], S. Thorwirth[1], K. Steenbakkers[2], T. Danowski[1], S. Brünken[2], O. Asvany[1], S. Schlemmer[1]*

[1]I. Physikalisches Institut, Universität zu Köln, [2]FELX Laboratory, Radboud University

Halogen-bearing molecules play an important role in organic chemistry where the use of halogenated reactants can help to elucidate the underlying mechanism of bi-molecular reactions in the gas-phase. Additionally, they have a strong influence in a number of important chemical reaction networks and molecules incorporating a halogen atom are known to exist in the interstellar medium. In this environment one of the key molecules is CH_3Cl which is predicted to form via gas-phase reactions of chloromethylium, CH_2Cl^+, and protonated methyl chloride, CH_3ClH^+. However, so far, no experimental vibrational or rotational gas-phase spectra of these two molecular ions are known, which are prerequisite for astronomical detection.

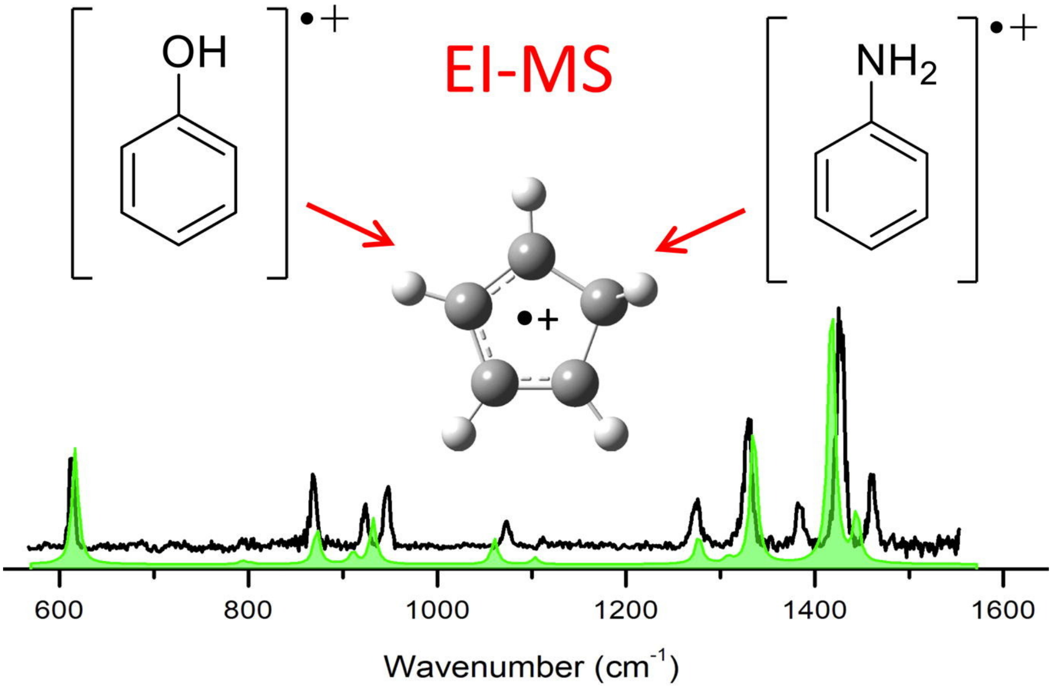
Here we present first experimental gas-phase IR spectra of CH_2Cl^+ and CH_3ClH^+, obtained using the FELion 22-pole ion trap experiment connected to the Free Electron Laser for Infrared eXperiments (FELIX) at Radboud University, Nijmegen. IR pre-dissociation spectra of CH_2Cl^+-Ne and CH_3ClH^+-Ne clusters were recorded in the range of 500 cm^{-1} up to 3000 cm^{-1} for isotopologs carrying both ^{35}Cl and ^{37}Cl. Spectroscopic assignment was performed based on complementary CCSD(T) calculations. Implications for future spectroscopic studies will also be discussed.

Cryogenic Messenger-IR Ion Spectroscopy Study of Phenol & Aniline Molecular Ions and of the common Fragment Ion $[C_5H_6]^{\bullet+}$ formed by EI-MS

M. Bast[1], D. Zeh[2], D. B. Rap[3], P. C. Schmid[1], S. Thorwirth[1], S. Brünken[3], S. Schlemmer[1]*, M. Schäfer[2]*

[1]I. Physikalisches Institut, Universität zu Köln, [2]University of Cologne, Department of Chemistry, Institute of Organic Chemistry, [3]Radboud University, Institute for Molecules and Materials, FELIX Laboratory

Molecular ions of phenol and aniline as well as the fragment ion at m/z 66 formed by electron ionization are examined with cryogenic messenger-IR ion spectroscopy and theory [1]. According to the recorded IR spectra aromatic ground state molecular ions of phenol and aniline are clearly identified. Similar to earlier reports our new set of spectroscopic and computational results supports the assumption that tautomeric molecular ions of phenol and aniline are only short-lived intermediates in the reaction path to the ultimate CO loss reaction product of phenol as well as the HNC loss product of aniline. Even the present cryogenic messenger-IR ion spectroscopy approach failed to collect spectroscopic evidence of the intermediate presence of these elusive tautomers of phenol and aniline molecular ions. However, our study clearly shows that the electron ionization mass spectrometry dissociation product ion of phenol and aniline at m/z 66 is the cyclopentadiene radical cation $[C_5H_6]^{\bullet+}$ for the presence of which convincing spectroscopic evidence could be collected proving the structure assignment and identification. All messenger-IR ion spectroscopy experiments were conducted on a cryogenic 22-pole ion trap with the use of neon atoms for tagging. The MS instrument was coupled to a free electron laser delivering wavelength tunable IR radiation for spectroscopy. Harmonic and anharmonic force field calculations complement the experiments and support band assignments of the recorded IR spectra and general data interpretation.



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Rovibrational spectroscopy of the CH^+-He and CH^+-He_4 complexes

T. C. Salomon[1], J. L. Doménech[2], P. C. Schmid[1], E. A. Michael[3], O. Asvany[1], S. Schlemmer[1]*

[1]I. Physikalisches Institut, Universität zu Köln, Köln, Germany, [2]Molecular Physics, Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain, [3]Department of Electrical Engineering, University of Chile, Santiago, Chile

A cryogenic 22-pole ion trap apparatus is used in combination with a table-top pulsed IR source to probe weakly bound CH^+-He and CH^+-He_4 complexes by predissociation spectroscopy at 4 K. The infrared photodissociation spectra of the C–H stretching vibrations are recorded in the range of 2720–2800 cm^{-1}. The spectrum of CH^+-He exhibits perpendicular transitions of a near prolate top with a band origin at 2745.9 cm^{-1}, and thus confirms it to have the theoretically predicted T-shaped structure [1] [2]. For CH^+-He_4, the C-H stretch along the symmetry axis of this oblate top results in parallel transitions, indicating a 4-membered Helium ring around the C-H bond.

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Exploring silicon chemistry in the electrical discharge of methyl phenyl silane using chirped-pulse Fourier-transform microwave spectroscopy.

G. Batra[1,2], D. Loru[1], A. L. Steber[1], M. Schnell[1,2]*

[1] Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany, [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität

Silicon is one of the most abundant elements in the Earth’s crust and is also prevalent in space in the form of gaseous molecules, interstellar dust, and ice grains. The first interstellar silicon was detected in 1971 in the form of SiO towards Sgr B2 [1]. Since then, more than 15 silicon containing molecules have been detected in various regions of the interstellar medium (ISM) and constitute approximately 7% of the total number of molecules detected in space to date [2].

Electrical discharge sources coupled with chirped-pulse Fourier-transform microwave spectroscopy have proved to be a great tool to produce in situ molecular ions, radicals, long chains, and ring structures of molecules of astronomical interest. In this work, we investigate the electrical discharge chemistry of methyl phenyl silane ($C_7H_{10}Si$), with the aim of studying the incorporation of silicon in the framework of complex organic molecules (COMs). The new species formed in the electrical discharge of methyl phenyl silane are probed using the Hamburg COMPACT spectrometer in the 2-12 GHz frequency regime [3]. The newly formed species can be assigned with rotational parameters required for interstellar searches with various radio telescopes like the Radio Telescope Effelsberg and Jansky Very Large Array (JVLA).

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First observation of the Comet-Tail ($A^2\Pi_i \rightarrow X^2\Sigma^+$) system in $^{12}C^{17}O^+$ and deperturbation analysis of the $A^2\Pi_i(v = 1)$ level

I. Piotrowska[1], R. Hakalla[1]*, W. Szajna[1], R. Kępa[1], P. Kolek[1], A. Para[1], S. Ryzner[1], M. I. Malicka[2]

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland, [2]The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, Rzeszów, Poland

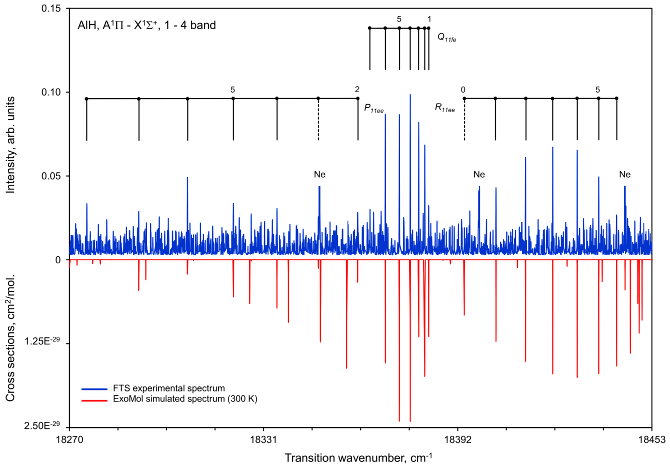
In the emission spectrum of the $^{12}C^{17}O^+$ molecule new observations and analyses were performed. Three bands (1-0, 1-1 and 1-2) of the Comet–Tail ($A^2\Pi_i \rightarrow X^2\Sigma^+$) system, including 1215 spectral transitions in the 16 950 to 22 000 cm^{-1} region, were recorded with the Fourier-transform spectrometer (BRUKER IFS 125-HR). As a source of the studied spectrum an air-cooled, carbon hollow-cathode lamp was used. A precise deperturbation analysis of the $A^2\Pi_i(v=1)$ level brought about the discovery of weak but non-negligible, $A^2\Pi_i(v=1) \sim X^2\Sigma^+(v=11)$ perturbation, of a complex, spin-orbit, spin-electronic and ***L***-uncoupling character. As a result, 15 deperturbed molecular parameters of both $A^2\Pi_i(v=1)$ and $X^2\Sigma^+(v=1,2)$ states were obtained. 11 of 15 these constants were delivered for the first time. The other 4 parameters for the lower $X^2\Sigma^+(v=1,2)$ levels were also calculated with an accuracy of one order of magnitude better than these determined previously. Moreover, the rovibronic term values of the $A^2\Pi_i(v=1)$ and $X^2\Sigma^+(v=0,1,2)$ levels were determined. A percentage $^2\Pi$ character of the $A^2\Pi_i(v=1)$ and $X^2\Sigma^+(v=11)$ levels was considered in detail.

FT emission spectroscopy of the $A^1\Pi$ – $X^1\Sigma^+$ system of AlH

W. Szajna[1], R. Hakalla[1], I. Piotrowska[1], P. Kolek[1], A. Para[1], S. Ryzner[1], M. I. Malicka[2], R. Kępa[1]

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland, [2]The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, Rzeszów, Poland,

This work presents the wide measurements of the high-resolution Fourier transform emission spectra of the of the $A^1\Pi$ – $X^1\Sigma^+$ system of aluminum hydride in the visible region. The AlH molecules were formed and excited within a water-cooled aluminum hollow-cathode lamp in the presence of 2.5 Torr of Ne and a trace amount of NH_3. The eight bands, 0–0; 1; 2 and 1–0; 1; 2; 3; 4, of the A – X transition were recorded with an instrumental resolution of 0.03 cm^{-1}. The 1–4 band band was recorded for the frst time since 1954 [1]. In total, 259 rotational frequencies were measured with an absolute accuracy of about 0.0020 cm^{-1}. The current data have been combined with the available measurements of the the ro-vibrational bands by Deutsch et al. [2], Yamada and Hirota [3], White et al. [4] and Ito et. al [5] as well as with the pure rotational frequency calculated from the data of Halfen and Ziurys [6,7]. As a results, the wide set of the improved molecular constants of the $X^1\Sigma^+$, v=0–8 and $A^1\Pi$, v=0;1 states of AlH has been obtained. A very weak perturbation [8] at $A^1\Pi$, v=1, J = 5 was confirmed.



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Deperturbation analysis of the $A^1\Pi(v = 2)$ level in $^{12}C^{18}O$

M. I. Malicka[1], S. Ryzner[2], A. N. Heays[3], N. de Oliveira[4], R. W. Field[5], W. Ubachs[6], R. Hakalla[2]*

[1]The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, Rzeszów, Poland, [2]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland, [3]J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic, [4]Synchrotron SOLEIL, Orme de Merisiers, St. Aubin, France, [5]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, USA, [6]Department of Physics and Astronomy, and LaserLaB, Vrije Universiteit, Amsterdam, Netherlands

The $A^1\Pi(v = 2)$ level of $^{12}C^{18}O$ was re-examined based on high-accuracy experimental data comprised of 541 line frequencies obtained by two Fourier-transform spectroscopic techniques. The absorption spectrum of $A^1\Pi – X^1\Sigma^+(2, 0)$ was measured with the VUV-FT spectrometer at the DESIRS beamline of the SOLEIL synchrotron with frequency accuracies of 0.01 cm^{-1}. While visible emission spectra of $B^1\Sigma^+ – A^1\Pi(0, 2)$ and $C^1\Sigma^+ – A^1\Pi(0, 2)$ were obtained with a Bruker IFS-125HR spectrometer at the University of Rzeszów with frequency accuracies of 0.005 and 0.01 cm^{-1}, respectively.

All new experimental molecular lines, and additional VUV-FT data of $^{12}C^{18}O$ $B^1\Sigma^+ – X^1\Sigma^+(0, 0)$ and $C^1\Sigma^+ – X^1\Sigma^+(0, 0)$ bands [1] were included in a deperturbation analysis of the $A^1\Pi(v = 2)$ level using PGOPHER program [2]. Finally, 11 deperturbed molecular constants and 6 interaction energies were obtained, along with, 110 experimental ro-vibrational term values of the $A^1\Pi(v = 2)$ levels and perturbing $e^3\Sigma^-(v = 4)$, $I^1\Sigma^-(v = 3)$, $a'^3\Sigma^+(v =12)$, $d^3\Delta(v = 7)$ levels. A significant, indirect influence of $a^3\Pi$ on the $A^1\Pi$ state was detected for the first time in $^{12}C^{18}O$ and has therefore been included in the final fit by taking into account the simultaneous $a^3\Pi(v = 13) \sim [e^3\Sigma^-(v = 4), d^3\Delta(v = 7), a'^3\Sigma^+(v = 12)] \sim A^1\Pi(v = 2)$ spin-orbit/spin-electronic/***L***-uncoupling and spin-orbit interactions as well as the $a^3\Pi(v = 13) \sim [D^1\Delta(v = 3), I^1\Sigma^-(v = 3)] \sim A^1\Pi(v = 2)$ spin-orbit and ***L***-uncoupling interactions. The new results provide a significantly improved description of the $A^1\Pi(v = 2)$ level in $^{12}C^{18}O$ and its complex intra-molecular structure compare to the previous data [3-4].

This work is a continuation of the research on the $A^1\Pi$ state of carbon monoxide conducted by our team in recent years [1,5-7].

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High-resolution rotational spectroscopy of large steroid hormones

S. V. Caliebe[1,2], P. Pinacho[2], M. M. Quesada-Moreno[3], S. Zinn[2], M. Schnell[2,1]*

[1]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, [2] Deutsches Elektronen-Synchrotron (DESY), [3]Departamento de Química Inorgánica, Universidad de Granada

We have studied a series of steroid hormones by chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy following the earlier study on 17β-estradiol ($C_{18}H_{24}O_2$)[1]. These hormones can be viewed as large molecules for rotational spectroscopy, consequently their investigation is a challenging task. The molecules were studied in the gas phase using a supersonic expansion, which allows for an isolated and cold environment, and their spectra were recorded in the 2-8 GHz frequency region. Here, we present the rotational spectrum of androsterone ($C_{19}H_{30}O_2$), for which the lowest energy structure was found. Furthermore, we re-investigated the spectra of 17β-estradiol and beside the three already reported conformers we found two unknown species. These were then assigned as two conformers of estrone ($C_{18}H_{22}O_2$), which is a precursor in the synthesis of 17β-estradiol and forms an equilibrium with it.

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High-resolution measurements of rovibrational spectra of methyl iodide in the 3.3 µm range using frequency comb Fourier transform spectroscopy

A. Hjältén[1], I. Sadiek[2], F. Senna Vieira[1], C. Lu[1], M. Stuhr[3], A. Foltynowicz[1]*

[1]Umeå University, Department of Physics, 901 87 Umeå, Sweden, [2]Leibniz Institute for Plasma Science and Technology (INP), 17489 Greifswald, Germany, [3]University of Kiel, Institute of Physical Chemistry, 24118 Kiel, Germany

Methyl iodide, CH_3I, plays an integral role in atmospheric chemistry. Apart from this, it has a number of industrial and agricultural applications, where its toxic properties pose a health threat. The development of laser-based detection of this species has so far been hampered by the lack of accurate spectral parameters and absorption cross-section data. In this work, we use comb-based Fourier transform spectroscopy (FTS) to measure and assign broadband high-resolution spectra of methyl iodide around 3.3 µm [1]. A liquid sample of CH_3I was evaporated into an evacuated 76-m multipass cell by its room temperature vapor pressure. The absorption spectra were measured using a mid-infrared frequency comb produced by difference frequency generation (DFG) based on a Yb:fiber comb with a repetition rate of 125 MHz [2]. The idler, centered at 2975 cm^{-1}, had a bandwidth of 360 cm^{-1}, sufficient to simultaneously cover several vibrational bands, including the symmetric C-H stretch ν_1 band and the asymmetric C-H stretch ν_4 band. Individual Doppler-broadened absorption lines were resolved using the sub-nominal sampling-interleaving scheme in the FTS [3].

We simulated the ν_4 fundamental band and the nearby $\nu_3 + \nu_4 - \nu_3$ hot band using PGOPHER [4] and parameters from previous microwave [5, 6] and FTIR [7] measurements. We assigned 2603 lines to the ν_4 band and 831 lines to the hot band. Floating the upper state parameters and fitting to the assigned lines yielded standard deviations (observed-calculated) of 0.00034 cm^{-1} and 0.00084 cm^{-1} for the two bands respectively, which is a significant improvement compared to earlier FTIR-based work [7]. In addition, we retrieved line intensities of 157 isolated lines of the ν_4 band by multispectral fitting to spectra recorded at different partial pressures of CH_3I.

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Detailed analysis of the infrared spectrum of $SiF_{4:}$ an update

V. Boudon[1], L. Manceron[2,3]

[1]Laboratoire Interdisciplinaire Carnot de Bourgogne, [2]Synchrotron SOLEIL, AILES Beamline, [3] MONARIS

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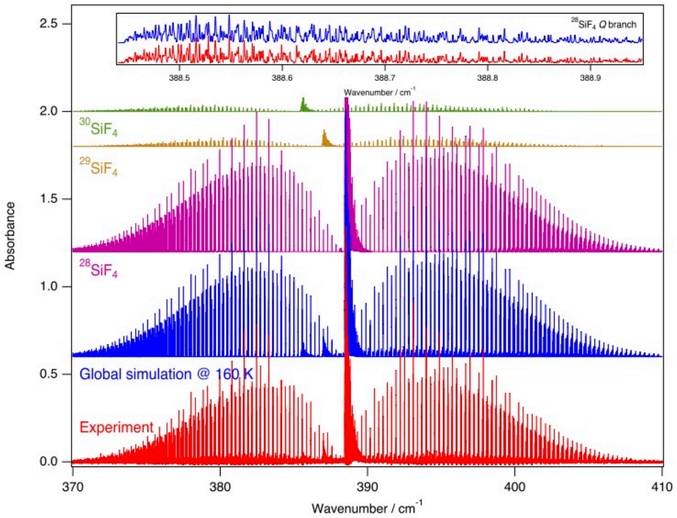
Silicon tetrafluoride (SiF_4) should be a normal trace component of volcanic gases. However, a better knowledge of spectroscopic parameters is needed for this molecule in order to derive accurate concentrations.

We undertook an extensive high-resolution study of its in-frared absorption bands, for the there isotopologues in natural abundance: $^{28}SiF_4$(92.23 %), $^{29}SiF_4$ (4.67 %) and $^{30}SiF_4$ (3.10 %) [1]. We present here an update of this study. It includes a new global fit with consistent parameter sets for the ground and all fundamental states (the Figure presents the ν_4 bending fundamental region), thanks to newly recorded far-IR and mid-IR spectra.



All existing rotational line data have been included. The $2\nu_4$ band of $^{28}SiF_4$ could also be analyzed in detail. A first rough estimate of the dipole moment derivative for the ν_3 band has been performed, leading to to an integrated band intensity which is consistent with literature values, around 680 km/mol [1]. The isotopic dependance of band centers and Coriolis parameters has been studied, thanks to simple formulas recently established [2].

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The Rotationally Resolved Infrared Spectrum of Linear Dialuminum Monoxide, Al-O-Al

E. Döring[1], D. Witsch[1], A. A. Breier[1], J. Gauss[2], G. W. Fuchs[1]*, T. F. Giesen[1]*

[1]Institute of Physics, University of Kassel, Kassel, Germany, [2]Institut für Physikalische Chemie, Universtität Mainz, Mainz, Germany

Cosmic dust forms via nucleation processes in the vicinity of evolved stars. Considering many of the initial nucleation steps are not well understood, yet, the investigation of small di- and triatomic molecules at radio or infrared wavelengths in stellar environments can help elucidating the dust formation processes. Especially molecules made of refractory material, like aluminum, are thought to act as seed molecules for dust grains, since they condense already at temperatures well above thousand Kelvin. Because Al_2O has no permanent electric dipole moment it can not be detected at radio wavelengths but it has a unique infrared ro-vibrational spectrum around 10µm.

In this work the gas phase spectrum of the symmetric linear dialuminum monoxide Al-O-Al is investigated in our laboratory. We recorded the rotationally resolved infrared absorption spectrum of Al_2O by using a frequency modulated quantum cascade laser in combination with Herriott-type multipass optics. By laser ablating an aluminum rod the molecules were produced and rotationally cooled down to around 120K by purging the ablation plume with a N_2O/He buffer gas mixture which subsequently underwent an adiabatic expansion into a vacuum chamber. The spectrum reveal a line intensity alteration due to the spin-statistical weight induced by two identical spin 5/2 ^{27}Al atoms. Beside the fundamental ν3 = 1-0 transition also five hot band transitions could be observed.

This allowed high-precision molecular constants to be determined and a *l*-type resonance to be analyzed. The transition frequencies presented here will enable the astrophysical search for this molecule in space.

Line intensities of the 01111-00001 magnetic dipole absorption band of $^{12}C^{16}O_2$: laboratory measurements

V. I. Perevalov[1], Y. G. Borkov[1], A. M. Solodov[1], A. A. Solodov[1]

[1]V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev square, 634055 Tomsk, Russia

The spectra of carbon dioxide in the 3.3 μm region were recorded at three pressures using Bruker IFS 125 HR Fourier transform spectrometer and a 30 m base multipass gas cell of V.E. Zuev Institute of Atmospheric Optics SB RAS. Several lines of the 01111-00001 ($\nu_2+\nu_3$) magnetic dipole band of $^{12}C^{16}O_2$ were detected and their line intensities were measured. The uncertainties of the measured line intensities are between 4% and 25%. The vibrational transition magnetic dipole moment was fitted to the observed line intensities. The fitted value of the vibrational transition magnetic dipole moment of $0.71(1)\mu_N$ is substantially smaller than the value of $0.96\mu_N$ obtained in the result of the analysis of the Martian atmosphere spectra [1,2] (here μ_N is the nuclear magneton). Using the known set of the effective Hamiltonian parameters and fitted value of the vibrational transition magnetic dipole moment the list of the line parameters of this band was generated for the HITRAN database. In addition the line intensities of the R-branch of the electric dipole 01111-00001 band of the $^{16}O^{12}C^{18}O$ isotopologue were measured for the first time.

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Ionization energy of the metastable 2 $^1S_0$ state of ^{4}He from Rydberg-series extrapolation

G. B. Clausen[1], P. Jansen[1], S. Scheidegger[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich

In a very recent breakthrough in first-principles calculations of two-electron systems, Patkóš, Yerokhin and Pachucki (PRA **103**, 042809 (2021)) have performed the first complete calculation of the Lamb shift of the helium 2 $^3S_1$ and 2 ^3P_J triplet states up to the term in α^7m. Whereas their theoretical result of the frequency of the 2 ^{3}P ←2 ^{3}S transition perfectly agrees with the experimental value, a more than 10σ discrepancy was identified for the 3 ^{3}D ← 2 ^{3}S and 3^{3}D ← 2^{3}P transitions, which hinders the determination of the He^{2+} charge radius from atomic spectroscopy that is necessary to complement the recent α-particle charge radius determination using muonic helium (J. Krauth *et al.*, Nature **589**, 527531 (2021)).

We report on the determination of the ionization energy of the metastable 2 $^1S_0$ state of helium (960'332'040.491(32) MHz) by Rydberg-series extrapolation based on the frequencies of 21 transitions from the 2 $^1S_0$ state to *n*p Rydberg states with principal quantum number *n* in the range between 24 and 102, yielding a relative uncertainty of $3\text{x}10^{-11}$. A one-photon (~312 nm) excitation scheme is used for Rydberg-state excitation of metastable He atoms in a doubly skimmed supersonic beam.

The absolute frequency calibration is achieved using a frequency comb referenced to a GPS-disciplined Rb clock. This absolute measurement is used in combination with the 2 $^3S_1$ ← 2 $^1S_0$ interval measured by van Rooij *et al.* (Science **333**, 196 (2011)) and the 2 ^{3}P ← 2 $^3S_1$ interval measured by Zheng *et al.* (PRL **119**, 263002 (2017)) and Cancio Pastor *et al.* (PRL **92**, 023001 (2004)) to derive experimental ionization energies of the 2 $^3S_1$ state 1'152'842'742.637(32) MHz) and the 2 ^{3}P centroid energy (876'106'247.017(32) MHz). These values reveal disagreements with the α^7m Lamb shift prediction by 6.5σ and 11σ, respectively, and support the suggestion by Patkóš *et al.* of an unknown theoretical contribution to the Lamb shifts of the 2 ^{3}S and 2 ^{3}P states of He.

The ν_1 vibrational mode of HC_3O^+ observed at high spectral resolution

S. Thorwirth[1], O. Asvany[1], M. E. Harding[2], S. Schlemmer[1]

[1]I. Physikalisches Institut, Universität zu Köln, [2]Karlsruhe Institute of Technology

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Following-up on our recent infrared photodissociation (IRPD) spectroscopic detection of the linear Ne-tagged HC_3O^+ molecular ion [1], the C-H stretching mode ν_1 of bare HC_3O^+ has now been studied at high spectral resolution. The spectrum was observed using a 4 K cryogenic ion trap apparatus at Cologne (COLtrap) and a cw optical parametric oscillator using the method of laser-induced inhibition of complex growth (LIICG) with helium as tagging agent. Fifteen rotational-vibrational transitions were observed, covering *P*(8) to *R*(6). The band origin is found at 3237.1 cm^{-1} and hence blueshifted by some 5 cm^{-1} compared to that of the HC_3O^+-Ne weakly bound complex probed earlier in the IRPD study.

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Laboratory spectroscopy and astrophysical search for small nitrogen-bearing organics

L. Bizzocchi[1,2]

[1]Scuola Normale Superiore, Pisa (Italy), [2]Max-Planck-Institute für extraterrestrische Physik

The recent new discoveries of small organics in the interstellar medium (more than 30 in the last three years) has enlarged the range of interest to increasingly complex species. Here a focus on a small group of N-containing molecules is presented. They are: propargylimine HC≡C-CH=NH, allylimine CH2=CH-CH=NH, 2-aza-butadiene CH2=N-CH=CH, 2-amino-acrylonitrile H2N-CH=CH-C≡N, and methylcyanamide CH3-NH-C≡N. All these molecules exhibit an interesting reactivity, both in gas-phase and on dust grain surface, thus hinting for their possible role in the route toward complex, biologically relevant, species.

We present new extensive investigations of the millimetre/sub-millimetre spectra of these targets obtained with frequency-modulation absorption spectrometers located in Bologna and at MPE/Garching. The new set of spectroscopic constants has been used to search for their molecular signatures in the spectral survey of the quiescent giant molecular cloud G+0.693-0.027, nearby the Galactic centre. Besides the secure identification obtained for propargylimine [1], a tentative detection of both allylimine conformers is reported.

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Large Amplitude Torsions in Nitrotoluene Isomers studied by Rotational Spectroscopy and Quantum Chemistry Calculations

A. Cuisset[1], A. Roucou[1,4], M. Goubet[2], I. Kleiner[3], S. Bteich[2]

[1]Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France, [2]Laboratoire PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France, [3]Laboratoire Inter-universitaire des systèmes atmosphériques (LISA), CNRS UMR7583, Université Paris-Est Créteil et Université de Paris,, [4]Institut de la Matière Condensée et des Nanosciences (IMCN), Universite´ catholique de Louvain, Louvain-la-Neuve, Belgium

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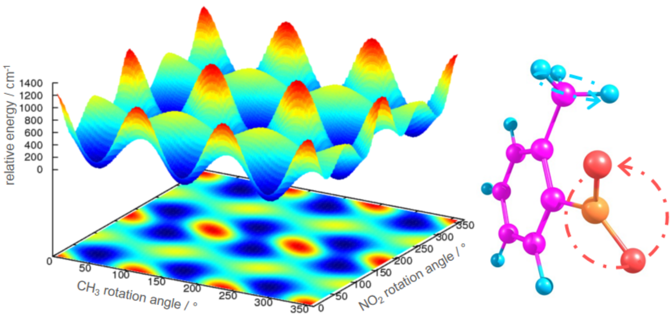
The monitoring of gas phase mononitrotoluenes is crucial for defence, civil security and environmental interests since they are used as taggant for TNT detection. Rotational spectra of the three isomers of nitrotoluene have been recorded at low and room temperatures using a supersonic jet Fourier Transform microwave (MW) spectrometer and a millimeter-wave frequency multiplier chain, respectively. Supported by quantum chemistry calculations, the spectral analysis of pure rotation lines in the vibrational ground state has allowed to characterise the rotational energy, the hyperfine structure due to the ^{14}N nucleus and the internal rotation splittings arising from the methyl group. An anisotropic internal rotation of coupled -CH_3 and -NO_2 torsional motions was identified for the ortho isomer by quantum chemistry calculations and discussed from the results of its MW analysis. The study of the internal rotation splittings in the spectra of three NT isomers allowed to characterise the internal rotation potentials of the methyl group and to compare them with other mono-substituted toluene derivatives in order to study the isomeric influence on the internal rotation barrier. [1,2]



Anisotropic internal rotation of coupled -CH_3 and -NO_2 torsional motions identified in the ortho isomer of mono-nitrotoluene.

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Frequency stabilization of a 4.7 THz Quantum Cascade Laser using a methanol gas line

S. Mahdizadeh[1], M. Justen[1], U. Graf[1], K. Jacobs[1], J. Stutzki[1]

[1]1. Physics Institute, University of Cologne, Zülpicher Str. 77, 50937 Köln, Germany

We present the frequency stabilization of a 4.7 THz Quantum Cascade Laser (QCL) to a methanol gas line. QCL is producing 5 mW of THz power and is cooled down to 33.5K, mechanically isolated from and thermally connected with first stage of a pulse-tube cryogenic cooler. The methanol gas line which is located at frequency close to 4.785 THz plays the role of frequency discriminator. Laser radiation is passed through a gas cell of 31 cm long and then is coupled to the Hot Electron Bolometer (HEB), here acting as a total power detector. Sending the current output of HEB into a lock-in amplifier while using the modulator waveform as reference signal, the lock-in output is used as error signal to close the control loop and eliminate unwanted frequency modulation of the QCL. As a result, frequency modulation from many of the pulse-tube harmonics could be considerably reduced, among which the peak frequency deviation of 1.1 MHz from fundamental frequency at 1.72 Hz could be decreased by a factor of 10.

A Theoretical Ro-Vibrational Line List of H_2Cs Using a new Approach to Construct the Exact Kinetic Energy Operator

T. Mellor[1,4], A. Yachmenev [2,5], S. N. Yurchenko [3]

[1] UCL Department of Physics and Astronomy , [2]Center for Free-Electron Laser Science, Deutsches ,
[3] UCL Department of Physics and Astronomy ,Universi, [4]UK, [5]Center for Ultrafast Imaging,
Universität Hamburg,

A procedure to generate the exact kinetic energy operator in valence coordinates, based on Sørensen’s method [1] for constructing non-rigid Hamiltonians, is presented. This method was applied to the thioformaldehyde (H 2 CS) molecule, where the TROVE program was used to compute ro-vibrational energy levels and transition intensities. A line list up to J=105 was produced. Yachmenev et al.'s ab initio PES [2] is refined with the MARVEL approach using ~4300 non-unique transitions from 10 sources. The exact kinetic energy operator itself was produced using the symbolic computation program Mathematica and acted as TROVE input. This method has previously been applied to the linear molecule CO2. [3]

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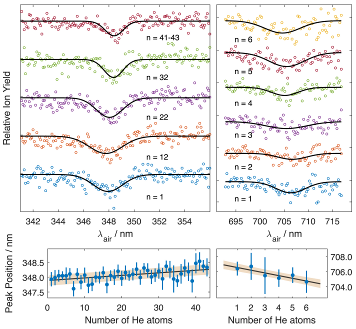
Helium-Tagging Action Spectroscopy Using Helium Nanodroplets: Electronic Spectroscopy of Cold Anthracene Cations

A. Schiller[1], M. Meyer[1], P. Martini[1], F. Zappa[1], S. A. Krasnokutski[2], P. Scheier[1]*

[1]Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria, [2]Laboratory Astrophysics Group of the MPI for Astronomy at the University of Jena, Germany

Diffuse interstellar bands (DIBs) are absorption features in the visible and infrared range, originating from dense parts of the interstellar medium. Although their discovery dates back a century[1] and some ~500 DIBs are known today, the species causing these features remain widely unknown. The first and so far only successful identification was only made in 2015 when C_{60}^+ was confirmed to be the carrier of two intense DIBs in the IR by Campbell et al[2] via helium-tagging spectroscopy in a cryogenic trap. Despite the weak interaction of the tag with the solvated species, a small wavelength shift compared to the gas-phase transition remains. Helium nanodroplets present an alternative tool for producing cold helium-tagged ions with up to ~100 attached helium atoms. This allows for a systematic analysis of the tag-induced shift as a function of the number of attached helium atoms. The progression of this shift can be extrapolated to obtain an accurate prediction of the gas-phase transition wavelength[3,4].

We employed a recently improved experimental setup to perform electronic spectroscopy on helium-tagged cold anthracene cations (He_nAn^+) using the described method[5]. Anthracene ($C_{14}H_{10}$) is a small polycyclic aromatic hydrocarbon which was considered to be a good candidate to be a potential DIBs carrier. We detected two bands of An^+ near 348nm and 707nm that are suitable for comparison with astronomical observations, but did not find a coincidence with any known DIBs.



This work was supported by the Austrian Science Fund FWF, project numbers I4130 and P31149 as well as the Max Plank Institute for Astronomy and the Deutsche Forschungsgemeinschaft DFG (grant No. KR 3995/4-1).

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High-resolution spectroscopy with quantum cascade laser frequency combs

M. Mangold[1], P. Allmendinger[1], J. Hayden[1], F. Eigenmann[1], O. Browet[2], M. Lepère[2], M. Gianella[3], L. Emmenegger[3], A. Hugi[1]

[1]IRsweep AG, Switzerland, [2]University of Namur, Research unit Lasers and Spectroscopies (LLS), Belgium, [3]Empa, Laboratory for Air Pollution / Environmental Technologies, Switzerland

Optical frequency comb spectroscopy has proven a very useful tool for high-resolution molecular spectroscopy. Frequency combs based on quantum cascade lasers offer the possibility to easily explore the mid-infrared spectral range (4-12 µm) and allow for microsecond time resolution. However, they suffer from very large repetition frequencies (~10 GHz) which make them seemingly unsuitable for high resolution spectroscopy.

Recently, several techniques to overcome this limitation have been developed. In what we call the *rapid-sweep* technique, the two frequency combs are simultaneously modulated to cover the gap between adjacent comb modes [1]. The simultaneous modulation and the inherently high time-resolution of quantum cascade laser dual-comb spectroscopy makes it possible to retrieve the full high-resolution spectrum in only 6 ms. Furthermore, the data throughput of this approach has been significantly improved to allow for continuous, broadband, high-resolution spectroscopy [2].

In the so-called *step-sweep* mode, the lasers are each individually modulated in small steps. This method guarantees an accurate knowledge of the frequency axis by directly measuring the optical step size from the heterodyne beat signal [3]. The step-sweep technique is best adapted to studies of molecular line parameters such as line strength, line position and line broadening [4].

Recently, the high time resolution of quantum cascade laser dual-comb spectroscopy has been used in combination with the *step-sweep* technique. This has allowed to measure broadband high-resolution spectra of sub-millisecond-lived samples. The resolution and wavenumber accuracy obtained using this technique have been assessed in a study of cold gases in supersonic beams [5, 6]. Here, we present an overview of the technological details and some representative measurements for each of the three measurement modes.

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Linewidth measurement of Interband-Cascade Lasers

M. Siciliani de Cumis[1], S. Borri[2], S. Viciani[2], F. D'Amato[2], P. De Natale[2]

[1]Agenzia Spaziale Italiana, [2]Istituto Nazionale di Ottica

In spectroscopy and metrology, the mid-infrared and THz regions are crucial due to the presence of strong molecular absorption lines. While the mid-IR to the THz region [1] are covered by Quantum Cascade Lasers (QCL), the region below 4 µm cannot be investigated by using this kind of lasers due to their internal structure. Indeed, the 3-4 µm region is particularly interesting due to the presence of fundamental molecular bands for life science and astrophysics (e.g. the O-H and C-H stretching bands). Interband Cascade Lasers (ICLs) emit from 3 to 6 µm, and are characterized by low-power consumption and compact dimensions. For these reasons they are a valid alternative to QCLs especially for in-field applications or for space missions [2,3]. Their application for high-resolution spectroscopy experiments or frequency metrology strongly depends on the achievable frequency stability and linewidth.

For the structure and internal carrier generation and transport processes, ICLs are different from other semiconductor lasers. However, a full evaluation of their potential has not been possible yet, due to a poor understanding of their internal physics lacking also of a theoretical model.

Here, we present a study regarding frequency stability and quantum-limited operation of such lasers. We characterized an ICL emitting at 4.6 µm, performing noise measurement achieving measured 10-kHz intrinsic linewidth [4]. The frequency noise features allow to mark the difference with other semiconductor lasers like bipolar diode lasers and QCLs, thus giving a first insight on the internal physics of these devices. Our analysis also enabled to estimate the linewidth enhancement factor of these devices. These results are very promising both for new-generation devices with improved performance and for high resolution molecular spectroscopy experiments in the 3-6 µm range.

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Demonstration of a Long-Pulse Fourier-Transform Limited Laser System exploited for High-Resolution Spectroscopy in Argon

H. Herburger[1], U. Hollenstein[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich

We demonstrate a laser system providing user-designed laser pulses with durations tunable from 10 ns to 1 µs and pulse energies up to 680 mJ per pulse at a repetition rate of 25 Hz and at a wavelength of 1064 nm. This radiation is frequency doubled in an LBO crystal yielding 532 nm radiation with pulse energies of 90 mJ per pulse. The frequency-doubled laser is used as a pump source for a dye amplification line seeded by the output of a commercial continuous-wave ring dye laser. This system enables us to generate 10 ns to 120 ns long pulses with a Gaussian temporal profile in the visible range of the electromagnetic spectrum with output energies of up to 5 mJ per pulse. We also generate long pulses of UV radiation (pulse energies up to 500 µJ, pulse length up to 85 ns) by frequency doubling in a BBO crystal.

The properties of the laser system are illustrated in measurements of the one- and two-photon Rydberg spectrum of atomic argon in the $3p^54s[3/2]_2\ ^3P_2$ and $3p^54s'[1/2]_0\ ^3P_0$ metastable states. Metastable argon is generated in a supersonic beam using a dielectric barrier discharge. We have recorded spectra of Rydberg series of Ar below the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds. We use the long lifetimes of the former series to characterize the bandwith of the laser system and determine the autoionization linewidth and line shapes of the later series for comparison with earlier work [1].

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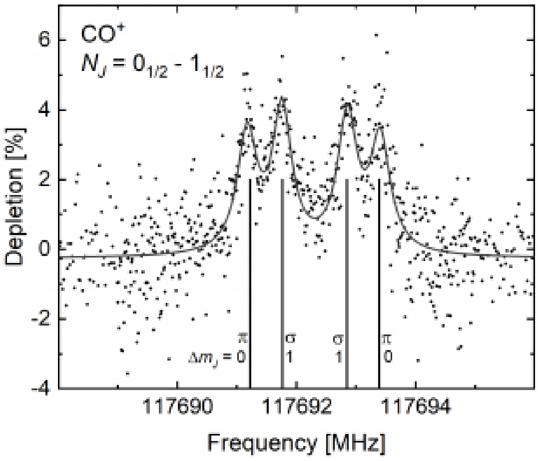
The Zeeman effect in CO$^+$ observed with rotational action spectroscopy

A. N. Marimuthu[1], K. Steenbakkers[1], B. Redlich[1]*, S. Brünken[1]*

[1]FELIX Laboratory, Radboud University, Nijmegen

The fine-structure components of the *N* = 0 --> 1 and *N* = 1 --> 2 transitions of CO$^+$ ($^2\Sigma^+$) have been measured using the action spectroscopic technique ROSAA (Rotational State-dependent Attachment of rare gas Atoms) [1,2] in a cryogenic 22-pole ion trap. The recorded high-resolution spectra show resolved Zeeman splittings caused by the Earth's magnetic field, which are analyzed with an effective Hamiltonian approach. The ROSAA signal intensity intrinsically depends on a difference in the ternary attachment rate of He atoms to the molecular ion for different rotational levels, and is also influenced by experimental conditions such as temperature, excitation power, and helium number density. Numerical simulation results of the underlying kinetics and excitation processes are compared to the observed CO$^+$ spectra.



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Spectroscopy of molecular glow discharge products using REMPI

V. Grigorian[1], K. Vávra[2], S. Schwetje[1], M. A. Kaufmann[1]*

[1]University of Kassel, [2]University of Chemistry and Technology Prague

Diffuse interstellar bands (DIBs) are a century old spectroscopic mystery, which can be observed in the UV and visible spectral range along many astronomic sightlines [1]. The source of these rather diverse spectral features, ranging from narrow and distinct to very shallow and broad, are largely unknown. Due to the rich variety of carbon chemistry in the interstellar medium, polycyclic aromatic hydrocarbons (PAHs) contribute most likely to over 500 unidentified diffuse signals. A first breakthrough was achieved in 2015 with the assignment of C_{60}^+ as one of the carriers of some DIBs [2]. Nevertheless, the majority of DIBs remains still unassigned.

In this work a glow discharge plasma is used in order to produce different molecular species in a molecular beam by introducing simple carbonaceous precursor molecules within a carrier gas, as demonstrated by T.Motylewski and H.Linnartz 1999 [3].
Resonance enhanced multi-photon ionization schemes (REMPI) combined with a time of flight mass spectrometer provide high measurement sensitivity and are predestined for spectroscopy of samples with unknown composition.
We present spectra of molecular species created by a glow discharge nozzle and observe their vibrionic transitions in the UV spectral range.

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Chirped-pulse Fourier-transform microwave spectroscopy study of 2,4,6-cycloheptatriene-1-carbonitrile

L. Pille[1,2], B. E. Arenas[1,2], G. Batra[1,2], M. Schnell[1,2]*

[1] Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany , [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel

An entirely new area of organic chemistry in the interstellar medium (ISM) has opened up because of the astronomical detection of CN-functionalized ring molecules. After the detection of five-membered [1] and six-membered [2] rings, similar and more complex organic compounds are of interest for astrochemical investigations. The seven-membered ring 2,4,6-cycloheptatriene-1-carbonitrile is such an example, with a permanent electric dipole moment of about 4.3 Debye. With the use of segmented chirped-pulse Fourier-transform microwave spectroscopy (CP-FTMW) [3], we investigated the rotational spectrum of this molecule in the 18-26 GHz region. In this contribution, we will discuss the precise rotational constants obtained for the lowest energy conformer and the determination of the gas-phase structure based on the assignment of ^{13}C and ^{15}N isotopologues. The accurate line lists produced from these analyses will facilitate searches for these species in various regions of the ISM.

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Mid Infrared CW Cavity Ring Down Spectroscopy in a Supersonic Jet

F. Peterß[1], T. Neumann[1], G. W. Fuchs[1]*

[1]Institute of Physics, University of Kassel

The cavity ring down (CRD) technique is an absorption based highly sensitive spectroscopic analyzing method based on the multiple reflection of light between a pair of highly reflective mirrors (>99.99%). Here, we report about our progress in building up a mid-infrared CRD experiment where we use a tunable cw-OPO laser system operating between 2.6µm - 4.0 µm to probe a supersonic jet of gas containing molecules produced in a discharge or laser ablation source. While the cavity ring down technique itself is well known at optical wavelengths, the application to mid infrared wavelengths for spectroscopy proved to be difficult but is now constantly improving due to the availability of suitable tunable laser sources and sufficiently reflective mirrors. The mid infrared region around 3µm, where our CRD mirrors have their best reflectivity, is interesting from a molecular spectroscopy point of view, because -O-H, -N-H and ≡C-H stretching vibrations can be investigated in this wavelength region. First spectroscopic results and a brief technical characterization of our CRD setup will be presented on the poster.

High-Resolution Spectroscopic Measurements of Cold Samples in Supersonic Beams using a QCL-Comb Spectrometer

U. Hollenstein[1], J. A. Agner[1], A. Pitt[2], H. Andreas[2], K. Keppler[1], M. Mangold[2], F. Merkt[1], M. Quack[1]

[1]Laboratorium für Physikalische Chemie, ETH Zürich. Vladimir-Prelog-Weg 2, CH-8093 Zürich, Switzerland, [2]IRsweep AG, Laubisruetistrasse 44, CH-8712 Stäfa, Switzerland

Optical frequency comb spectroscopy has proven a very useful tool for high resolution molecular spectroscopy. Frequency combs based on quantum cascade lasers (QCL) offer the possibility to easily explore the mid-infrared spectral range (4 µm to 12 µm), but suffer from very large repetition frequencies (~ 10 GHz) which make them seemingly unsuitable for high resolution spectroscopy.

Here, we present techniques to overcome this limitation. We have employed the combined advantages of high temporal (< 4 µs) and high spectral resolution to measure the IR spectra of CF_4 and $CHCl_2F$ in pulsed, skimmed supersonic beams. The low rotational temperature of the beams and the narrow expansion cone after the skimmer enabled the recording of spectra of cold samples with high resolution. The spectra cover the range from 1200 cm^{-1} to 1290 cm^{-1} and the narrowest lines have a full width at half maximum of 15 MHz, limited by the Doppler effect. The results demonstrate the potential of QCL dual-comb spectroscopy for broadband (> 60 cm^{-1}) acquisition of spectra at high resolution (< 15 MHz) and high sensitivity in the mid-infrared range. The power of the new technology is demonstrated by comparison with previous results on these molecules obtained by FTIR and diode laser spectroscopy of seeded cw and pulsed supersonic jets. [1-3]

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Variational calculations of a ro-vibrational spectrum of ethane using an *ab initio* potential energy surface and a symmetry-adapted G_{36}(EM) basis set

S. N. Yurchenko [1], T. M. Mellor[1]

[1]Department of Physics and Astronomy, London, UK

Recently, we presented a detailed description of the G_{36}(EM) molecular symmetry group with a full set of irreducible representation matrices developed for constructing symmetry-adapted potential energy functions and basis set functions of ethane (C_2H_6) [1]. These transformation matrices and the symmetry adaption technique have been implemented as numerical procedures in the variational program TROVE [2] as part of computational approaches to the solution of the ro-vibrational Schrödinger equation. A self-consistent choice of the vibrational, torsional and rotational coordinates for ethane, satisfying the G_{36}(EM) symmetry requirements have been introduced and analysed in full detail. In this contribution we present calculations of rotation-vibrational energies of C_2H_6 based on an *ab initio* potential energy surface (PES) of the CCSD(T)/TZ-f12 level of theory computed on a grid of 30,000 geometries. The symmetry adapted G_{36}(EM) representation is used to build a Taylor-type parametrised expansion for our *ab initio* PES of ethane. We will show that due to the large number of the degrees of freedom, the variational calculations are extremely difficult to converge. Possible solutions for the curse of the dimensionality problem in case of ethane calculations will be discussed. Our goal is to compute a line list for C_2H_6 as part of the ExoMol project [3].

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Cold HSOH in a supersonic jet expansion

J. A. Baldeh[1], A. A. Breier[1], E. Döring[1], B. Waßmuth[1], G. W. Fuchs[1], T. F. Giesen[1]*

[1]Laboratory Astrophysics, University of Kassel, Heinrich-Plett Str. 40, 34132 Kassel, Germany

style="text-align: justify;">Since the experimental prove of the 3-wave mixing process on a molecular racemic sample [1], the goal of enantiomeric separation, conversion and purification by enantioselective excitation is achievable.

The precondition is that the molecular energy structure is understood very precisely, hence, typically this process is performed on the molecular rotational degree of freedoms. Theoretical investigation suggests also that the process can be applied to the molecular vibrational modes [2]. To verify this idea the chiral molecule HSOH is suitable, where its two enantiomers are connected by the dynamics of its internal rotation[3].

Unfortunately, the common production methods of the radical HSOH results in hot high resolution IR spectra leading to difficulties in the assignment process of its vibrational states. From our experience in producing HOOH in a supersonic jet, we developed the first steps in producing cold HSOH by means of electrical discharge techniques combine with a supersonic jet expansion. This production method might also foster the enantioselective excitation in the IR region.

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New developments in CP-FTmmW spectroscopy

A. Körner[1], P. Stahl[1], T. F. Giesen[1]*, G. W. Fuchs[1]*

[1]Institute of Physics, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Understanding the chemistry of space requires astrophysical observations with modern telescopes such as ALMA (Atacama Large Millimetre Array). The comparison of these radio-astronomical data with high-resolution rotational spectra from the laboratory allows the identification of molecules and the evaluation of their abundance in the investigated areas.

Chirped pulse Fourier-transform (CPFT) spectroscopy became a standard technique to efficiently produce such data with high-frequency resolution[1] and large signal-to-noise-ratios. Due to recent technological developments, CPFT spectroscopy became also feasible in the millimetre wave (mmW) regime.

We present a new automatised high-resolution CPFTmmW spectrometer, which operates in the range of 100-112.5 GHz with a typical excitation power of 600mW and a peak power of 1W. The spectrometer was used in a flow cell, with supersonic jet applications, and a multi-pass optic.

Furthermore, we want to combine these features with laser ablation and discharge sources to produce (transient) molecules, which are of astrochemical relevance, e.g. TiO_2. Their fingerprints might facilitate the search for these molecules in astronomical spectra. First results will be presented.

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Efficient quantum-state population transfer in molecular rotation by ultrashort laser pulses

D. Ikeda[1], Y. Ohshima[1]*

[1]Department of Chemistry, School of Science, Tokyo Institute of Technology, Japan

Efficient population transfer between molecular eigenstates is a powerful tool for exploring molecular science. For instance, an ensemble with molecules residing in a single quantum state can be beneficial in experiments pursuing highly sensitive spectroscopy and state-to-state chemistry. Multi-step excitation is required for accessing arbitrary states with high internal energies. When adopting conventional approaches, *e.g.*, adiabatic passage using narrow-band light sources with high spectral coherence [1], multi-step excitation needs elaborated optical setups with multiple lasers. From the view of ultrafast coherent control, the use of broadband laser has realized excitation with 60% efficiency [2]. The challenge is the suppression of excitations to other (non-target) states. Here, we numerically demonstrate methods for almost complete population transfer between rotational states using ultrashort laser pulses and also report some experimental results.

We simulated the excitation efficiency by solving the time-dependent Schrödinger equation for the rotational Raman excitation in diatomic molecules (CO and NO) by non-resonant light pulses. For realizing efficient population transfer, two identical pulses with a time delay were examined to control the population by wave-packet interference (WPI). The single pulse with a variable pulse duration was assumed to be generated by applying a linear frequency chirp to a Gaussian pulse (100 fs duration, centered at 800 nm). We explored conditions that realize almost complete population transfer, taking the delay time, peak intensity, and pulse duration as optimized parameters. We found some excitation conditions with over 90% efficiency.

In the experiment, we demonstrated WPI excitation in nitric oxide (NO) molecules. The schematic is shown in Fig.1(a). Adiabatically cooled NO molecules were excited by a pair of picosecond near-infrared laser pulses (790 nm, 1.8 ps, ~100 mJ/mm^2). The delay time between the double pulses was adjusted to give constructive WPI. After about 50 nanosecond delay, two-photon resonant ionization spectrum ($A^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$, 0-0 band) was recorded by an irradiation of a frequency-tunable nanosecond ultraviolet laser pulse (~226 nm), as shown Fig.1(b). The efficiency for the excitation from J = 1/2 to J = 3/2 was evaluated to be 68%. The probable origin of differences between numerical and experimental efficiencies will be discussed.

In addition to the WPI approach, we also examined a new method implementing a pair of chirped pulses with partial temporal overlap. The utilities of the method will also be discussed.

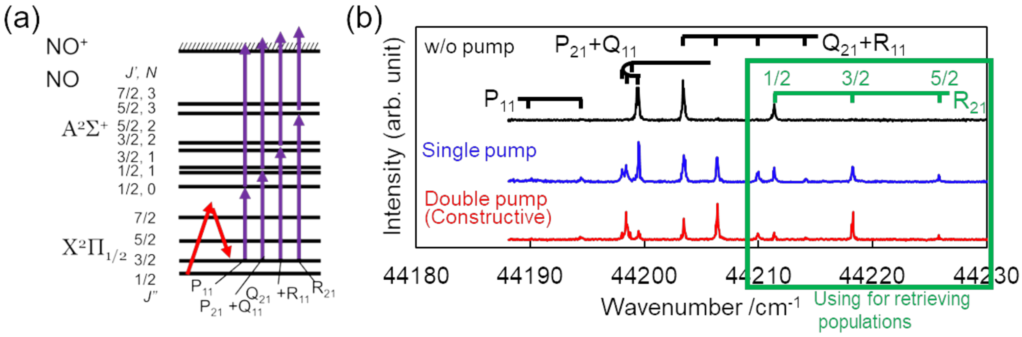

Fig.1 (a) Experimental scheme, (b) REMPI spectra of NO (A-X) transitions

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Coherent control of torsional vibration in biphenyl derivatives by impulsive stimulated Raman scattering

M. Nikaido[1], K. Mizuse[2,1], Y. Ohshima[1]*

[1]Department of Chemistry, School of Science, Tokyo Institute of Technology, Japan, [2]Department of Chemistry, School of Science, Kitasato University, Japan

With recent advances in ultrashort laser technology, many studies using intense nonresonant laser fields have been conducted to control vibrational or rotational wave packets. In particular, control of large-amplitude low-frequency vibration is important because such vibration may cause a substantial change in molecular structure. For instance, the torsional motion of biphenyl has deserved much attention since the chirality and physical properties of the molecule depend on its torsional angle. In this study, we coherently excite torsional vibration of substituted biphenyl derivatives by the interaction with ultrashort laser fields, and the resultant vibrational excitation is monitored by recording resonant two-photon ionization (R2PI) spectrum. We further adopt double-pulse excitation to control vibrational state distribution via wave-packet interference.

The adiabatically cooled molecular sample of 2-fluorobiphenyl is irradiated by the fundamental output from femto-second Ti:Sapphire laser. This pump pulse induces vibrational excitation through impulsive stimulated Raman scattering. With an appropriate delay after the pump-pulse irradiation, the S_1-S_0 excitation spectrum of the molecules is recorded via R2PI with the doubled output of a nanosecond dye laser (~280 nm). A progression with almost constant spacings appears in the R2PI spectrum without the pump pulse. It has been assigned to that of the torsional mode from the vibrational ground state, *i.e.*, v = 0 (v being the quantum number of the torsional mode in the electronic ground state) [1]. When the pump pulse is introduced, the new bands appear and they are assigned to the progression from v = 1. These observations indicate that impulsive stimulated Raman excitation of torsional vibration is realized. We also conduct a double-pump pulse experiment, where a pair of pulses are implemented for excitation. The experimental results show the oscillatory change of the transition intensity from v = 1 while scanning the delay between the pump pulses, as shown in Figure 1 (a). Fourier transformation of this result presents the energy differences between the eigenstates of torsional vibration, as shown in Figure 1 (b). Furthermore, adjusting the double pump delay, we succeeded in observing the transition from v = 2, which are scarcely observed with the single pump pulse.

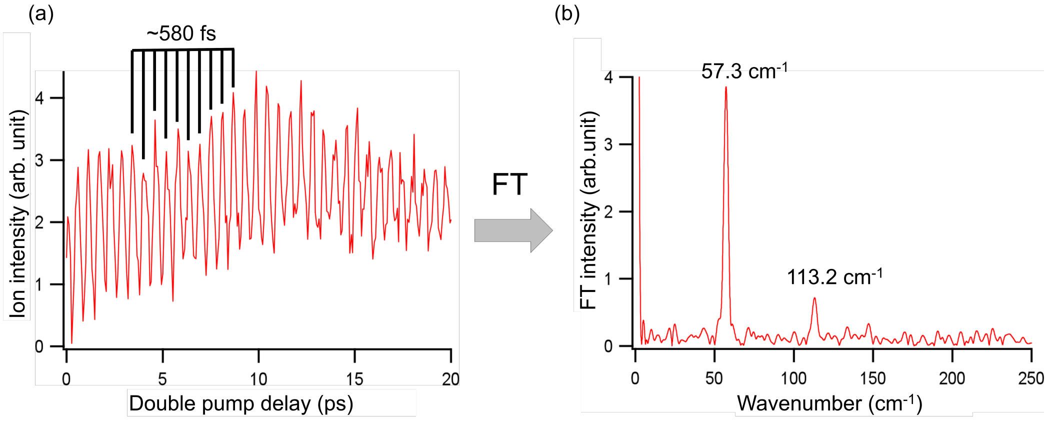

Figure 1. (a) Change of transition intensity from v = 1. (b) Fourier transformation of (a).

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An algorithm to retrieve the instrument line shape of a high resolution Fourier transform spectrometer

T. Bertin[1], J. Vander Auwera[1]*

[1]SQUARES, C.P. 160/09, Université Libre de Bruxelles, 50 avenue F.D. Roosevelt, 1050 Brussels, Belgium

Fourier transform spectra include the non negligible contribution of the instrumental line shape (ILS) of the spectrometer, even at high resolution. To avoid biasing the information retrieved from these spectra, a reliable modeling of the actual ILS of the spectrometer is required. Several methods have been developed to retrieve the ILS from Fourier transform spectra of isolated lines at low pressure, either partially [1] or completely [2, 3], including its wavenumber dependence for the ACE-FTS [4].

The present method builds upon the work of Boone and Bernath [4]. It includes a modeling of the wavenumber dependence of the ILS adapted to high resolution laboratory Fourier transform spectrometers and accounts for the loss of information on the ILS resulting from the molecular line shape. The method, implemented in a simple python script, will be presented and its performance compared with LINEFIT [2].

Acknowledgements: T. Bertin thanks the FRIA (Belgium) for a PhD fellowship. This work is financially supported by the Fonds de la Recherche Scientifique - FNRS (Belgium).

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LLWP - A new Loomis-Wood Software at the Example of Propanone-$^{13}C_1$

L. Bonah[1], O. Zingsheim[1], S. Thorwirth[1], H. S. Müller[1], F. Lewen[1], J. Guillemin[2], S. Schlemmer[1]*

[1]I. Physikalisches Institut, Universität zu Köln, [2]ENSC, Université de Rennes

Spectra of complex molecules are dense and complicated, especially if isotopologues, low-lying vibrationally excited states, hyperfine structure or other interactions are present. Analysis of these spectra can be difficult due to line confusion. One approach to accommodate this challenge are Loomis-Wood plots (LWPs), which are a visual aid for displaying series of transitions in a spectrum in order to ease assignments. Programs utilizing LWPs exist already in the literature, e.g. AABS [1], Pgopher [2] and LWW [3]. Here, we present a newly developed software which focuses on being intuitive and user friendly while simultaneously allowing for fast and confident assignments of molecular spectra. The software is called LLWP and is written in Python. The core functionality and selected features are presented on the example of first results of the analysis of isotopically enriched propanone-$^{13}C_1$ ($^{13}CH_3COCH_3$), which was synthesized as its signal at natural abundance only allowed for a very limited analysis [4, 5]. The software and its full documentation are available at ltotheois.github.io/LLWP.

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Reconstruction of Term Diagrams without using a Model Hamiltonian

S. Brackertz[1], S. M. Kristkeitz[1], O. Asvany[1], S. Schlemmer[1]*

[1]I. Physikalisches Institut, Universität zu Köln

The fundamental Ritz combination principle [1] originally found for atoms has also been applied to molecules as a method to reconstruct the energy states from measured lines without relying on any model Hamiltonian. In 2006 Nesbitt and coworkers [2] proposed to apply it to protonated methane, CH_5^+, which was first done in 2015 [3] and extended in 2017 [4] by our group. Currently, we are elaborating this method to a universal, easy to use tool which can be used for arbitrary spectra. Essentials of the program and examples, including the floppy He-H_3^+ system, will be discussed.

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Characterizing home-built chirped-pulse spectrometers for complex molecules of astrophysical interest

B. Heyne[1], M. Hermanns[1], S. Schlemmer[1]*

[1]I. Physikalisches Institut, Universität zu Köln

We present our two chirped-pulse Fourier transform spectrometers operating in different frequency ranges. The instruments are designed to achieve high stability and sensitivity, which makes it possible to measure isotopic species of molecules in natural abundance.

One spectrometer operates between 12 and 26.5 GHz, which is interesting for rotational spectra of complex molecules, that are relevant for astrophysics, due to the matching frequency range of the Green Bank Telescope (290 MHz to 100 GHz). In a supplementary manner, many of the organic molecules present or possibly present in space have their maximum transition intensity in this region at cold temperatures. Another important field is the study of van der Waals complexes [1]. In a recent modification, we are using state-of-the-art RF modulation and detection technology to directly generate and receive signals in this frequency range, thus abandoning the up- and down-mixing processes of our previous chirped-pulse microwave spectrometer setup [2]. As a result, the tedious side-band separation is no longer needed. Moreover, the number of elements influencing the intensities is reduced to a minimum. To demonstrate the performance of our spectrometer, we will present the spectra of 13C isotopologs of n-propyl cyanide observed in natural abundance. We have also detected the fingerprint-like rotational spectra of 4'-methylacetophenone, for which we used a nozzle attachment with a heated reservoir [3] to incorporate the less volatile, heavy molecules into the free jet. The performance of our instrument and example spectra will be discussed.

The other chirped pulse spectrometer is operational in the millimeter-wave range between 75 and 110 GHz, which is coincident with the Atacama Large Millimeter/Submillimeter Array (ALMA) Band 3. Besides the isotopologs in natural abundance, a high voltage DC discharge in combination with a supersonic jet is incorporated to observe fragments of molecules. For this application, the first tests were performed with methyl cyanide (CH3CN). We observed HCN as well as HNC discharge products. As the detector side of our instrument coincides in many aspects with our emission spectrometers [4,5], a comparison of chirped pulse measurements and emission spectroscopy will be discussed briefly.

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Rotational spectrum of acrylamide up to 480 GHz

L. Kolesniková[1], J. Koucký[1], E. R. Alonso[2], P. Kania[1], Š. Urban[1]*

[1]Department of Analytical Chemistry, University of Chemistry and Technology, Technická 5, Prague 6, 16628, Czech Republic, [2]Grupo de Espectroscopia Molecular (GEM), Edificio Quifima, Lab. de Espectroscopia y Bioespectroscopia, Parque Científico UVa, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, 47011, Spain

Many complex organic molecules have been detected in the interstellar medium among which amides are considered as models for the peptide linkage. Acrylamide ($CH_2CHC(O)NH_2$) bears in its backbone not only amide, but also vinyl functional group which is common structural motif in several interstellar compounds. This ranks acrylamide among interesting candidates for a search in the interstellar medium.

In the present work, the rotational spectrum of acrylamide was recorded between 75 and 480 GHz using two millimeter wave spectrometers [1, 2] and thousands of rotational transitions in the ground state and excited vibrational states were analyzed for the most stable *syn* form. In addition, a detailed analysis of the rotational transitions of the less stable *skew* conformer, for which a double-minimum potential for the skeletal torsion has been revealed, is reported. The new measurements and their analysis significantly extend the knowledge of the rotational spectrum of acrylamide [3] and enable to conduct a rigorous search for interstellar signatures of this amide by millimeter wave astronomy.

Acknowledgement

The funding from the Czech Science Foundation (GACR, grants 19-25116Y and 18-08667S) is gratefully acknowledged.

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Improvement of frequency measurement accuracy by accounting for standing-wave distortions in the lineshapes

E. Alekseev[1,2], V. Ilyushin[1,2]

[1]Institute of Radio Astronomy of NASU, Mystetstv 4, Kharkiv, Ukraine, [2]Quantum Radiophysics Department, V.N.Karazin Kharkiv National University, Kharkiv, Ukraine

As it is known presence of standing waves in an absorption cell leads to baseline variations, gives asymmetric distortions in observed lineshapes and limits possible accuracy of measurements. Application of frequency modulation of a source with lock-in detection in the receiving system allows to suppress considerably the baseline variations, but does not solve the problem of lineshape distortions due to standing waves. As it was pointed out by Pickett [1] because of reflections in a cell the detected signal is a linear combination of absorption and dispersion and namely this gives asymmetry of recorded lineshapes. Main problem here is unknown ratio between absorption and dispersion, especially when frequency modulation is used. We apply the Pickett's approach to analyze lineshape distortions due to presence of standing waves treating the unknown ratio between absorption and dispersion as a fitting parameter. This allows us to take into account observed lineshape distortions and provide a measurement accuracy at the sub-kHz level for the lines recorded with good signal-to-noise ratio.

In the talk the results of application of proposed approach to the conventional measurements with Doppler limited resolution as well as to Lamb-dip measurements will be demonstrated and discussed.[a]

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Cavity-enhanced sub-Doppler optical-optical double-resonance spectroscopy of methane using a frequency comb probe

V. Silva de Oliveira[1], I. Silander[1], L. Rutkowski[2], O. Axner[1], G. Soboń[3], K. K. Lehmann[4]*, A. Foltynowicz[1]*

[1]Department of Physics, Umeå University, Sweden, [2]Université de Rennes, CNRS, IPR-UMR 6251, F-35000 Rennes, France, [3]Faculty of Electronics, Wrocław University of Science and Technology, Poland, [4]Departments of Chemistry & Physics, University of Virginia, Charlottesville, VA, USA

Methane plays an important role in atmospheric science, combustion, and astrophysics. The near resonance of harmonic fundamental frequencies and the strong coupling of normal modes result in a complex energy level structure that is insufficiently understood for term values above 6200 cm^{-1}. To improve the accuracy of theoretical high-temperature line lists used to analyze spectroscopic data in combustion and astrophysics, firmly assigned experimental hot band transitions reaching levels above 8000 cm^{-1} are needed [1]. Optical-optical double resonance (OODR) spectroscopy is a powerful tool for selective measurement and assignment of hot band transitions. Recently, we employed OODR with a 3.3 μm continuous wave pump and a 1.67 μm frequency comb probe to measure and assign transitions in the $3\nu_3 \leftarrow \nu_3$ band of methane [2,3]. Using a Fourier transform spectrometer with sub-nominal sampling-interleaving scheme [4], we recorded probe spectra spanning 200 cm^{-1} of bandwidth with 2 MHz sampling point spacing and detected 36 probe $3\nu_3 \leftarrow \nu_3$ transitions with sub-Doppler resolution. We assigned the transitions by comparison to the line lists from the TheoReTS [5] and Exomol [6] databases.

In the first demonstration, the center frequency accuracy of the probe transitions was ~1.7 MHz, limited by the drift in the pump frequency stabilization. Moreover, the sample of pure CH_4 was contained in a single-pass cell, which yielded a maximum signal to noise ratio of 10 despite liquid nitrogen (LN_2) cooling that enhanced the absorption strength. Here, we report the implementation of an enhancement cavity for the comb probe, which improves the absorption sensitivity by more than two orders of magnitude without the need for LN_2 cooling, and reduces the influence of the pump frequency instability on the probe transition frequencies. In a cavity, the probe beam is simultaneously co- and counter-propagating with respect to the pump, so any instability in the pump frequency leads to a broadening rather than a shift of the center of the gravity of the probe transitions. We detect and assign previously unobserved weak sub-Doppler hot band transitions to the 9000 cm^{-1} energy levels with sub-MHz frequency accuracy. We assign the final energy levels by comparing combinations of pump and probe transitions reaching the same final states.

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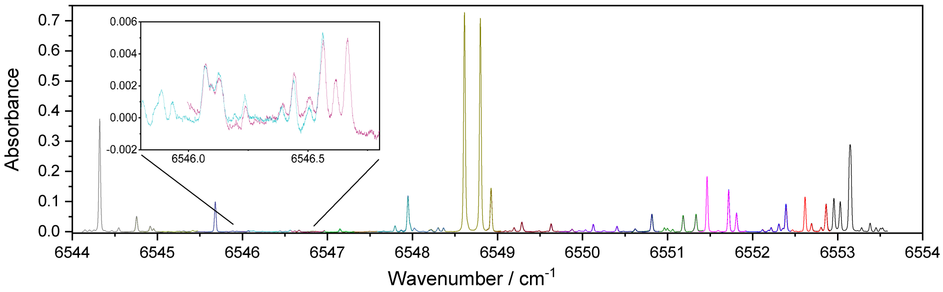
Ammonia line intensities measured by dTDLAS and their comparison to literature data in the 6544 to 6552 cm^{-1} region

A. Pogány[1], A. Kiuberis[2], O. Werhahn[1], V. Ebert[1,3]

[1]Physikalisch Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany, [2]Van Swinderen Institute for Particle Physics and Gravity, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands, [3]Reactive Flows and Diagnostics, Technische Universität Darmstadt, Otto-Berndt-Str. 3, 64287 Darmstadt, Germany

We have studied ammonia (NH_3) absorption lines within the tuning range of a DFB diode laser (6544 to 6552 cm^{-1}) using direct tunable diode laser absorption spectroscopy (dTDLAS)[1]. We determined line positions and approximate line intensities for all 126 observed lines. Metrological measurements with a thorough uncertainty analysis were performed in 4 selected sub-sets of the spectrum, to determine the intensity of 19 absorption lines with intensities in the 10^{-24} to 10^{-21} range. Our line intensity results for the stronger lines ($S_0 > 10^{-22}$) have uncertainties better than 5 % ($k = 2$).



We compared our results to literature data, including experimental data and ab initio calculations. The only comprehensive experimental study covering a broader wavenumber range was published by Sung et. al in 2012, which data are included in the HITRAN database. Besides this study, a few further experimental results were published on individual lines. We have done comparisons with ab initio line lists from the EXOMOL database: C2018 and CoYuTe.

Our results were found to be consistently 2-10 % lower than the data given in the HITRAN 2016 database. This is also the case for the 2 strongest lines (at 6548.61, 6548.80 cm^{-1}), which are routinely used in environmental NH_3 monitoring, we measured 7 % lower intensity for both lines. Independent NH_3 amount fraction measurements using a cavity ring-down instrument indicated that our line intensity results for these two lines are more accurate than previously reported experimental data [2]. Comparison to ab initio line intensities showed good agreement for most of the lines. The small number of published results in this wavenumber range, as well as the deviations between them point out that further research is needed to validate NH_3 line intensities in the NIR range.

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Program, Wednesday, September 1, 2021

Contributed Talks (G)

	High-Resolution (GA) Chair: Marie-Aline Martin-Drumel, CNRS, France	**Fundamental (GB)** Chair: Stefan Willitsch, Universität Basel, Switzerland	**Cluster (GC)** Chair: Sonia Melandri, Università di Bologna, Italy
12.00	***Dávid Ferenc***, ELTE «Relativistic and QED corrections for precision spectroscopy: state of the art and beyond»	***Hélène Fleurbaey***, Université Grenoble Alpes «Electric quadrupole and magnetic dipole transitions of CO_2 near 3.3 µm»	***Rizalina Tama Saragi***, University of Valladolid «Hydrogen Bonding Competition Between Water and Hydrogen Sulfide: MW Spectroscopy of Microsolvation of Benzyl Alcohol and Benzyl Mercaptan»
12.15	***Jonas Bruckhuisen***, Université du Littoral Côte d'Opale «High-resolution gas phase THz spectroscopy of the catechol low frequency modes involving an intramolecular hydrogen bond»	***Santeri Larnimaa***, University of Helsinki «Spectroscopy of radioactive molecules $^{14}CH_4$ and $H^{36}Cl$»	***Shefali Saxena***, King's College London «The chemistry of pah-$(H_2O)n$ clusters: a rotational spectroscopy study of azulene dimer and its interactions with water»
12.30	***Olivia Chitarra***, University Paris Saclay «Millimeter and sub-millimeter spectroscopic studies of astrophysical relevant radicals Illustration with the CH_2CN radical»	***Alexander A. Breier***, Universität Kassel «High-resolution spectroscopy of RaF - The search for New Physics beyond the Standard Model»	***Robin Glorieux***, Université catholique de Louvain «The N_2-water complexes studied in the 1 OD and 2 OH stretching regions»
12.45	***Semyon Vasilchenko***, V. E. Zuev Institute of Atmospheric Optics SB RAS «High resolution laser spectroscopy of the ozone molecule at the dissociation threshold near 1.2 µm»	***Szymon Wójtewicz***, Nicolaus Copernicus University «Doppler-free saturation spectra of weak CO_2 and O_2 transitions»	***Elias M. Neeman***, CNRS «The conformational landscape of 2-Pinen-10-ol and its water complex»
13.00	***Matthias Germann***, Umeå University «High-precision line positions of N_2O and CH_4 at 8 µm from optical frequency comb Fourier transform spectroscopy»	***Florian Lackner***, Graz University of Technology «Fluorescence Quenching and Enhancement in Rhodamine B Covered Au Nanoparticles in Helium Nanodroplets»	***Yang Zheng***, Chongqing University «Dual role of π electrons in furan mapped on the furan–CF_3Cl complex studied by rotational spectroscopy combined with theoretical calculations»
13.15	***Alberto Martin Santa Daria***, ELTE «Rovibrational computations for molecular dimers»	***Daniël B. Rap***, Radboud University «Infrared fingerprints of cationic benzonitrile·+ and its astrophysically important fragmentation pathway to ortho-benzyne·+»	***Pablo Pinacho***, Deutsches Elektronen-Synchrotron (DESY) «Gas-phase structure of borneol and isoborneol monomers and their microsolvated complexes»

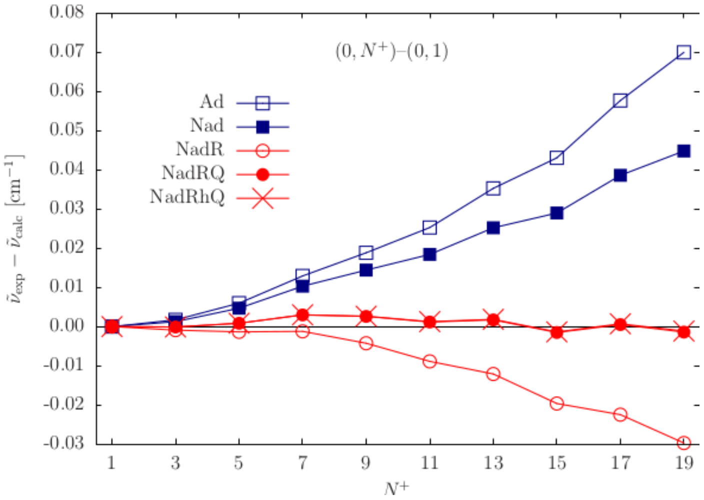
13.30	Break
	Invited Lectures (H) Chair: Harold Linnartz, University of Leiden, The Netherlands
14.00	***Isabelle Kleiner***, CNRS, Université Paris Est-Créteil et Université de Paris «Spectroscopy of large Amplitude Motions: from Interstellar Chemistry to Molecular Structures»
14.45	***Martin A. Suhm***, U. Goettingen «A doorway to vibrational resonance and other benchmarkable quantities in hydrate clusters»
15.30	Break
	Mini-Symposium: Laboratory Astrophysics and Spectroscopy (I) Chair: Sandra Brünken, Radboud University, The Netherlands
16.00	***Brett A McGuire***, Massachusetts Institute of Technology «Big Game Hunting: Tools and Techniques for Identifying Large Molecules in Space»
16.30	***Peter Schilke***, Universität zu Köln «Recent progress and challenges in analyzing complex astrophysical spectra»
17.00	***Oskar Asvany***, Universität zu Köln «Rotational Action Spectroscopy in Ion Traps»
17.30	***Christine Joblin***, University Toulouse 3 / CNRS «Deciphering the infrared emission of astro-PAHs: the interplay between laboratory experiments, quantum chemistry and modelling»
18.00	End of day 4

Relativistic and QED corrections for precision spectroscopy: state of the art and beyond

D. Ferenc[1], P. Jeszenszki[1], E. Mátyus[1]*

[1]ELTE, Eötvös Loránd University, 1117 Budapest, Pázmány Péter sétány 1/A

The quantitative understanding of high-precision molecular spectra requires the accurate computation of effects beyond the well-known non-relativistic Born–Oppenheimer picture. Few-electron molecules with low nuclear charge are of interest of both experimental and theoretical precision spectroscopy. The experiments together with theoretical computations are proposed as tests of our fundamental understanding of ordinary matter in the low-energy range. The underlying theory of the electromagnetic interactions, quantum electrodynamics (QED), can be applied in the computation of highly accurate rovibronic transitions. The non-relativistic QED (nrQED) framework allows us to include higher-order relativistic and radiative processes as corrections to the Schrödinger equation. In this contribution, applications of nrQED is presented for the rovibrational intervals in the *EF* $^1\Sigma_g^+$ excited electronic state of the hydrogen molecule and the rovibrational intervals of the $^4He_2^+$ molecular ion in its gorund electronic state [1]. In both cases, the agreement of the experimental transitions with the latest theoretical results was improved by several orders of magnitude [2,3]. The different contributions from the non-adiabatic, relativistic and QED corrections reveal an interesting interplay of the underlying physical phenomena.



Despite the excellent agreement for low-Z molecules there is still room for improvement on the theoretical side. The nrQED fails for molecules with medium and high nuclear charge, and the computation of higher-order correction terms is an increasingly complex numerical task. An alternative approach could be formulated by the solution of the Dirac–Coulomb(–Breit) equation by treating the relativistic and correlation effects on an equal footing [4]. The applicability of the method is not limited to low-Z species and it might serve as a complementary or possibly a competitive approach to nrQED.

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High-Resolution Gas Phase THz Spectroscopy of the Catechol low Frequency Modes involving an Intramolecular Hydrogen Bond

J. Bruckhuisen[1], G. Dhont[1], A. Roucou[1], A. Jabri[1], H. Bayoudh[1], T. T. Tran[1], M. Goubet[2], M. Martin-Drumel[3], A. Cuisset[1]*

[1]Laboratoire de Physico-Chimie de l’Atmosphère, Uni, [2]Laboratoire PhLAM - Physique des Lasers Atomes et , [3]Institut des Sciences Moleculaires d’Orsay

1,2-Benzenediol, commonly known as catechol, was investigated, an ortho substituted aromatic volatile organic compound (VOC) with two hydroxyl groups which, due to tunneling between two symmetrically equivalent structures, can interchangeably act as donor and acceptor in a weak hydrogen bond[1]. Catechol displays appreciable gas-phase reactivity and its monitoring in the atmosphere via rovibrational spectroscopy has a strong interest. We performed a rotationally resolved analysis of the “free” and “bonded” –OH torsion modes of the intramolecular H-bond using synchrotron-based FT-Far-IR spectroscopy at the AILES beamline of SOLEIL[2]. High level of theory anharmonic quantum chemistry calculations were required for the rovibrational assignment. Numerous series of hot bands involving the lowest vibrational energy modes are observed and a set of anharmonic parameters is proposed. Finally, using a millimeter-wave spectrometer[3] the room temperature Doppler limited rotational spectrum of catechol has been measured in the 70-220 GHz frequency range. Pure rotational lines belonging to the ground and the four lowest energy vibrationally excited states have been assigned. Splitting due to the tunneling were resolved for the free –OH torsion state and a global fit gathering the far-IR and millimeter-wave data provides the rotational parameters of the low-energy far-IR modes, especially those involving the intramolecular hydrogen bond.

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Millimeter and sub-millimeter spectroscopic studies of astrophysical relevant radicals Illustration with the CH_2CN radical

O. Chitarra[1], J. Spaniol[1], B. Gans[1], T. Hearne[1], J. Loison[2], O. Pirali[1], M. Martin-Drumel[1]*

[1]Institut des Sciences Moleculaires d'Orsay, [2]Institut des Sciences Moleculaires

Radical species are suspected to be involved in gas phase reactions occurring in the interstellar medium (ISM) [1] and their detection gives important insights about the chemistry happening in the ISM. To support ongoing searches of these species, laboratory spectroscopy is essential.

We developed several experimental set-up to study the high resolution spectra of radical species in a large spectral range covering the millimeter and sub-millimeter wave regions. In particular, we led new high-resolution studies in the (sub)millimeter-wave region on the cyanomethyl radical (CH_2CN) from 140 GHz up to 900 GHz. The pure rotational spectrum of the radical, produced by H abstraction of acetonitrile by F atoms, was recorded thanks to a frequency multiplication chain spectrometer. Previous laboratory investigations [2,3] only measured transitions up to about 300 GHz allowing for the detection of CH_2CN in the ISM [4]. We completed the spectroscopic characterization at higher frequencies and, in this talk, I will present our measurements yielding an improvement of its spectroscopic parameters.

With the aim of studying new reactive species, we are also developing a new set-up based on the coupling of a pulsed jet discharge with a commercial broadband W-band spectrometer (BrightSpec, 75-110 GHz). I will present the preliminary results we obtained on the CH_2CN radical observed at a rotational temperature of about 10 K.

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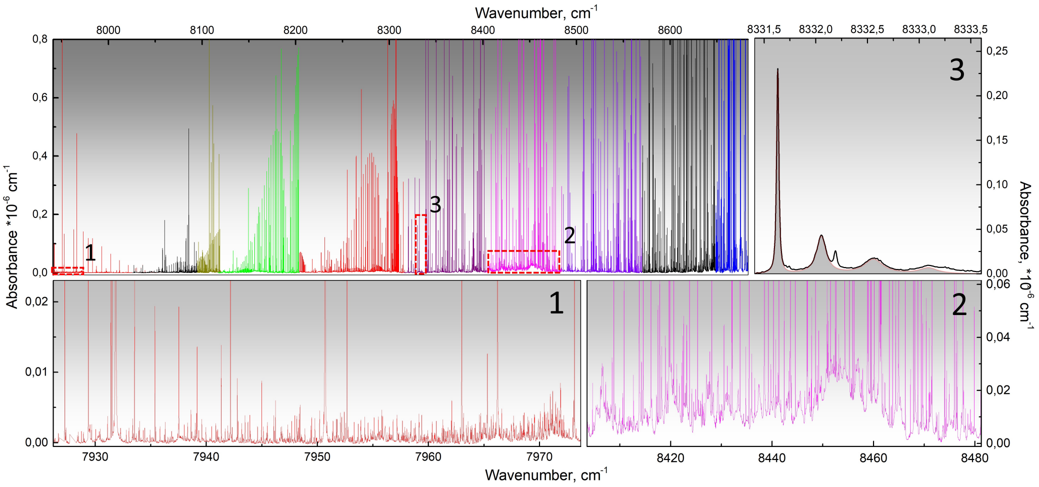
High resolution laser spectroscopy of the ozone molecule at the dissociation threshold near 1.2 µm

S. Vasilchenko[1,4], A. Barbe[2], E. Starikova[1,4], S. Kassi[3], D. Mondelain[3], A. Campargue[3], V. G. Tyuterev[4,2]*

[1]V. E. Zuev Institute of Atmospheric Optics SB RAS, 634055 Tomsk, Russia, [2]Groupe de Spectrométrie Moléculaire et Atmosphérique, UFR Sciences Exactes et Naturelles, Reims, France, [3]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, [4]Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 634050 Tomsk, Russia

High sensitivity spectra of the main ozone isotopologue were recorded using a cavity ring-down spectrometer in the region of 7920–8670 cm^{-1}, covering the range up to the dissociation threshold and above. The sensitivity of the recordings of the order of 2×10^{-11} cm^{-1} was achieved that makes it possible to detect high two energy combination bands up to ten vibrational quanta in electronic ground state [1]. Line positions and intensities are measured for these bands. These combination bands are superimposed to vibronic hot bands of the $^{16}O_3$ from the (100) and (020) electronic ground state levels to the excited $^3A_2$ triplet state which were analysed [2].

This work was supported by the Russian Science Foundation Grant No. 19-12-00171.



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High-precision line positions of N_2O and CH_4 at 8 µm from optical frequency comb Fourier transform spectroscopy

M. Germann[1], A. Hjältén[1], K. Krzempek[2], A. Hudzikowski[2], A. Głuszek[2], D. Tomaszewska[2], G. Soboń[2]*, A. Foltynowicz[1]*

[1]Department of Physics, Umeå University, 901 87 Umeå, Sweden, [2]Faculty of Electronics, Wrocław University of Science and Technology, 50-370 Wrocław, Poland

A number of small molecules of interest to atmospheric physics and astrophysics exhibit fundamental vibrational modes in the 8 µm spectral range. Spectroscopic detection of these molecular species in the Earth's atmosphere and in celestial objects requires accurate line lists. However, current spectroscopic databases in the 8 µm region are still largely based on conventional FTIR data with insufficient precision and accuracy. Much better precision and accuracy can be obtained using optical frequency comb spectroscopy, which provides a direct link of optical frequencies to radio frequency standards. Until now, the number of high-resolution comb-based measurements in the 8 µm range has been very limited, mostly because of the lack of reliable comb sources in this spectral region.

We recently developed an optical frequency comb Fourier transform spectrometer operating in the 8 µm range [1] based on a compact difference frequency generation optical frequency comb source [2] referenced to a GPS-disciplined Rb frequency standard. Employing the sub-nominal resolution sampling and interleaving technique [3,4], we acquired high-resolution low-pressure spectra of several vibrational bands of N_2O [1], a greenhouse gas and ozone depleting substance, and CH_4, a greenhouse gas and a constituent of (exo-)planetary atmospheres. The N_2O spectra cover a range of 1251 to 1318 cm^{-1} with a sampling point spacing of 9 MHz, while those of CH_4 span from 1240 to 1366 cm^{-1} at a point spacing of 14 MHz. From these spectra, we retrieved line positions with uncertainties on the level of a few hundred kHz – well below the precision of conventional FTIR-based studies. These may be used to validate and update the theoretical models at the basis of current spectroscopic databases.

We will present the comb-based spectrometer and the results obtained so far for N_2O and CH_4, and compare them with those of conventional FTIR spectroscopy, as well as a recent high-resolution study using a comb-referenced quantum-cascade laser [5].

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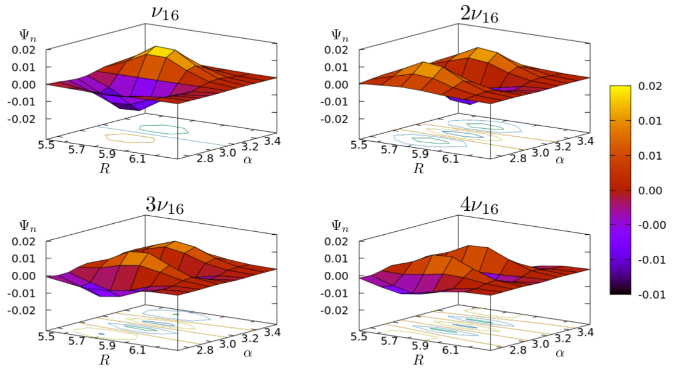
Rovibrational computations for molecular dimers

A. Martin Santa Daria[1], G. Avila[1], E. Mátyus[1]*

[1]ELTE, Eötvös Loránd University, 1117 Budapest, Pázmány Péter sétány 1/A

Fingerprint vibrations of the formic acid dimer, including all fundamental and several combination and overtone bands, have been reported with an experimental uncertainty of 1 cm^{-1} [1], while computational results deviate from experiment by 10–50 cm^{-1}. To clarify the origin of the large differences of theory and experiment, we have carried out [2] variational vibrational computations using curvilinear and normal coordinate vibrational models from 2 up to 10 fully coupled vibrational degrees of freedom using the GENIUSH computer program [3] and the full-dimensional potential energy surface (PES) developed by Qu and Bowman [4]. A good agreement is achieved with experiment for several fingerprint vibrational bands, but we have found indications for a necessary improvement of the PES before further vibrational computations (of higher dimensionality and/or including the tunneling mode) can be carried out.



Regarding the description of coupled large-amplitude motions, we elaborate on the convergence of rovibrational energies for systems where the amplitude of the wave function is significant in the singular region [5]. For this purpose, we benchmark the numerical convergence and computational efficiency of the black-box-type rovibrational procedure of GENIUSH with respect to a tailor-made dimer Hamiltonian approach [6] for the example of the intermolecular dynamics of the methane-water dimer.

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Electric quadrupole and magnetic dipole transitions of CO_2 near 3.3 µm.

H. Fleurbaey[1], R. Grilli[2], D. Mondelain[1], S. Kassi[1], A. Yachmenev [3,5], S. Yurchenko [4], A. Campargue[1]

[1]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, [2]Univ. Grenoble Alpes, CNRS, IGE, 38000 Grenoble, [3]Center for Free-Electron Laser Science, Universität Hamburg, [4] UCL Department of Physics and Astronomy , University College London, [5]Center for Ultrafast Imaging, Universität Hamburg

The recent detections of electric-quadrupole (E2) transitions in water vapor [1,2] and magnetic-dipole (M1) transitions in carbon dioxide [3,4] have opened a new field in molecular spectroscopy. While in their present status, the spectroscopic databases provide only electric-dipole (E1) transitions for polyatomic molecules (H_2O, CO_2, N_2O, CH_4, O_3...), the possible impact of weak E2 and M1 bands to the modeling of the Earth and planetary atmospheres has to be addressed. This is especially important in the case of carbon dioxide for which E2 and M1 bands may be located in spectral windows of weak E1 absorption. In the present work, a high sensitivity absorption spectrum of CO_2 was recorded by Optical-Feedback-Cavity Enhanced Absorption Spectroscopy (OFCEAS) in the 3.3 µm transparency window of carbon dioxide [5]. The studied spectral interval corresponds to the region where M1 transitions of the $\nu_2+\nu_3$ band of carbon dioxide were recently identified in the spectrum of the Martian atmosphere [3]. Here, in addition to M1 transitions, E2 transitions of the $\nu_2+\nu_3$ band could be detected by OFCEAS. This detection was performed on the basis of high accuracy *ab initio* predictions of the intensities of the E2 transitions [6]. This is the first laboratory detection of electric quadrupole transitions in carbon dioxide. The E2 intensity values (on the order of a few 10^{-29} cm/molecule) are found in reasonable agreement with *ab initio* calculations. We thus conclude that both E2 and M1 transitions should be systematically incorporated in the CO_2 line list provided by spectroscopic databases.

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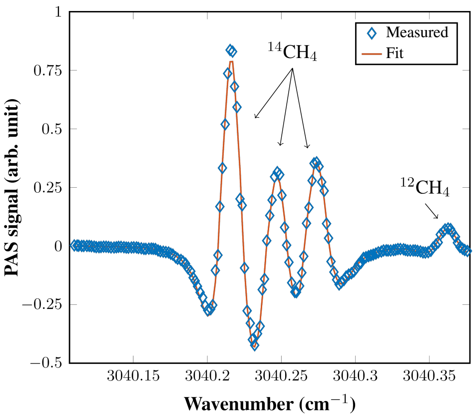
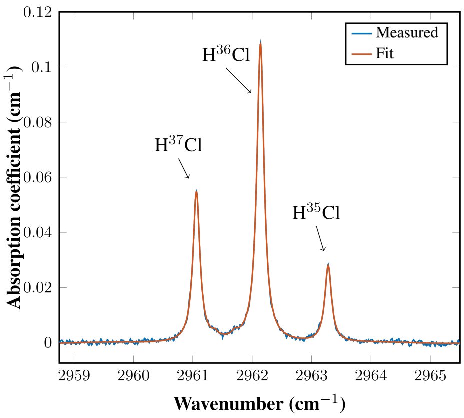
Spectroscopy of radioactive molecules $^{14}CH_4$ and $H^{36}Cl$

S. Larnimaa[1], L. Halonen[1], J. Karhu[1], T. Tomberg[1], M. Metsälä[1], G. Genoud[2], T. Hieta[3], S. Bell[4], V. Ulvila[2], M. Vainio[1,5]*

[1]University of Helsinki, Department of Chemistry, Helsinki, Finland, [2]VTT Technical Research Centre of Finland Limited, Espoo, Finland, [3]Gasera Ltd., Turku, Finland, [4]National Physical Laboratory, Middlesex, UK, [5]Photonics Laboratory, Physics Unit, Tampere University, Tampere, Finland

Spectroscopy of radioactive compounds has gained extensive interest in recent years. Especially radiocarbon dioxide $^{14}CO_2$ has been under thorough study with the motivation to develop optical instrumentation for its detection, for example, in nuclear facilities [1,2]. Another important radioactive molecule found in nuclear facilities is radiocarbon methane $^{14}CH_4$ [3]. In a preliminary work [4], we reported the first absorption spectrum of $^{14}CH_4$. More recently [5], we improved our results and reported high-resolution measurements and rotational analysis of the same fundamental asymmetric stretching vibrational band $\nu_3(F_2)$ of the molecule. We used a narrow linewidth, mid-infrared continuous-wave optical parametric oscillator combined with cantilever-enhanced photoacoustic spectroscopy and wavelength modulation spectroscopy to determine the line center wavenumbers of 43 rovibrational lines with 0.003 cm^{-1} uncertainty (95 % confidence level). In addition, a spectroscopic model was used in a non-linear least squares fit to confirm the experimental results and to determine the molecular constants. Our conference contribution presents this research on $^{14}CH_4$ and on our yet unpublished Fourier-transform infrared spectroscopy measurements of the fundamental and first overtone rovibrational bands of $H^{36}Cl$, a radioactive isotopologue of hydrogen chloride.





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High-resolution spectroscopy of RaF - The search for New Physics beyond the Standard Model

A. A. Breier[1], T. F. Giesen[1], R. Berger[2], R. F. Garcia Ruiz[3,4], S. G. Wilkins[4], S. M. Udrescu[3], K. T. Flanagan[5,6], G. Neyens[4,7]

[1]Laboratory Astrophysics, University of Kassel,Heinrich-Plett Str. 40, 34132 Kassel, Germany, [2] 3Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany, [3]Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA, [4]CERN, CH-1211 Geneva 23, Switzerland, [5]School of Physics and Astronomy, The University of Manchester, Manchester M13 9PL, United Kingdom, [6]Photon Science Institute, The University of Manchester, Manchester M13 9PY, United Kingdom, [7]KU Leuven, Instituut voor Kern- en Stralingsfysica, B-3001 Leuven, Belgium

The key role in understanding Nature is to validate our fundamental physical theories by experimental proofs. The Standard Model (SM) is a theoretical framework combining three out of the four fundamental interactions and arranging all known fundamental particles. However it cannot adequately explain everything, like the matter-antimatter asymmetry of our universe (baryogenesis)[1], which suggests the necessary existence of New Physics (NP) beyond the SM.
Typically, the idea of NP is tested by highly accelerated colliding particles, but nowadays, also table-top experiments evolve in sensitivity and precision to enable noticing deviations of observables from their SM predictions. The basic idea in most performed experiments is to measure the energy level structure of an atom or molecule very accurately by observing the transition frequencies.

Radium-containing molecules are the perfect testing environment for investigations of the SM and beyond [2]. In preparation to observe the small energy shift induced by NP, the underlying molecular motions have to be understood. Here, we report on our [3] spectroscopic investigation of the radioactive molecule RaF [4] at the ISOLDE radioactive ion-beam facility at CERN, leading to understand of its complex molecular motions and showing potential for efficient laser cooling, which will enable ultra-high-precision studies.

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Doppler-free saturation spectra of weak CO_2 and O_2 transitions

S. Wójtewicz[1], K. Bielska[1], J. Domysławska[1], A. Balashov[1,2], M. Słowiński[1], M. Bober[1], R. Ciuryło[1], D. Lisak[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland, [2]Institute of Applied Physics of the Russian Academy of Sciences, Ulyanov str. 46, 603950 Nizhny Novgorod, Russia

We present the Doppler-free saturated-absorption Lamb dip measurements of the CO_2 30012-00001 (1570 nm) as well as O_2 B band (690 nm) transitions. The spectra, measured at pressures ranging from about 0.3 to 20 Pa, were collected using three techniques: cavity ring-down spectroscopy (CRDS) [1], cavity mode-width spectroscopy (CMWS) [2], and cavity mode dispersion spectroscopy (CMDS) [3]. The spectrometers were linked to an optical frequency comb referenced to a hydrogen maser [4,5]. The retrieved line positions are characterized by uncertainties at the level of several kHz. The Doppler-free saturation spectra of magnetic dipole molecular transitions (O_2 B band) were measured for the first time. The results are compared with the available data [6, 7].

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Parallel Session: Fundamental, Contributed Talk (15min) **GB5**

Fluorescence Quenching and Enhancement in Rhodamine B Covered Au Nanoparticles in Helium Nanodroplets

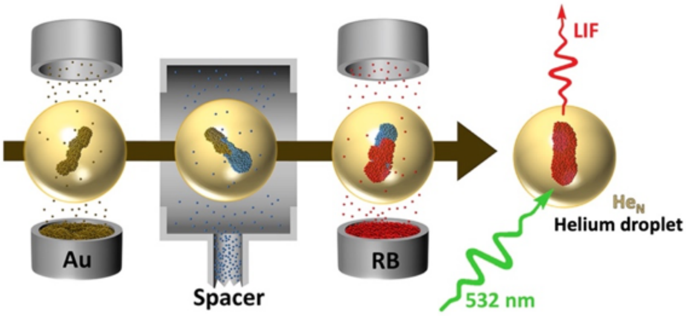
F. Lackner[1], R. Messner[1], W. E. Ernst[1]

[1]Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

class="MaintextAbstract">Nanoparticles comprising three different materials in a core@shell@shell structure are synthesized in cold helium droplets by sequential doping. [1,2]

Rhodamine B (RB) molecules form complexes in helium droplets that give rise to a strong fluorescence signal upon laser excitation at 532 nm, which enables an *in-situ* investigation of the synthesized structures. In the presence of Au core particles, the fluorescence collected from RB molecules is quenched, explained by an excitation transfer from excited molecules to the Au particles. This observation also indicates that both dopants are in contact and two-component Au@RB particles are formed. If an additional doping material is added to the helium droplets between the Au and RB pickup regions, the fluorescence is recovering again. This demonstrates that the added dopants form a spacer layer that separates the Au core from the RB molecules. Furthermore, it has been found that the fluorescence is recovered independent of the spacer material, Ar, isopropyl alcohol and hexane have been used, all of which are solid in the cold liquid helium environment. The synthesis process is sketched in the Figure.

The results demonstrate that it is possible to form nanoparticles consisting of three different layers in a Au@shell@RB configuration with the helium droplet synthesis technique.[1] Our current efforts are geared towards the spectroscopic characterization of other material combinations, focusing on helium droplets that contain plasmonic metals as major constituent.



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Infrared fingerprints of cationic benzonitrile$^{\cdot+}$ and its astrophysically important fragmentation pathway to ortho-benzyne$^{\cdot+}$

D. B. Rap[1], J. G. Schrauwen[1], B. Redlich[1], S. Brünken[1]*

[1]FELIX Laboratory, Radboud University

The radio-astronomical detection of nitrogen containing aromatic molecules such as neutral benzonitrile and cyano-naphthalene isomers in the Interstellar Medium (ISM) has sparked the interest in the investigation of both fragmentation and formation processes of these (polycyclic) aromatic hetero molecules [1–4]. Using a cryogenic ion trap apparatus coupled to an infrared free electron laser, we are able to structurally identify key ions of astrophysical relevance that take part in these processes [5,6]. By measuring the infrared fingerprint spectra using an action spectroscopic method involving rare-gas tagging, the structural characteristics of the ions can be determined by comparison with calculated infrared frequencies from quantum chemical computations. Here, we present the experimental infrared fingerprint of the benzonitrile radical cation and its major fragment $C_6H_4^{\cdot+}$ upon HCN loss. Quantum chemical computations of the infrared spectra of different $C_6H_4^{\cdot+}$ isomers enable us to assign the experimental structure to the non-planar ortho-benzyne radical cation. The attached rare-gas tag is shown to have a negligible effect on the majority of the vibrational band positions. The obtained structural information of benzonitrile$^{\cdot+}$ and its fragment ortho-benzyne$^{\cdot+}$ will extend the knowledge, and allows to speculate on the variety of structures that are likely to exist in the ISM besides the already detected neutral cyano-substituted cyclic molecules. Moreover, the accurate vibrational band positions can aid infrared observations in relevant astronomical environments such as photodissociation regions (PDRs) and planetary atmospheres.

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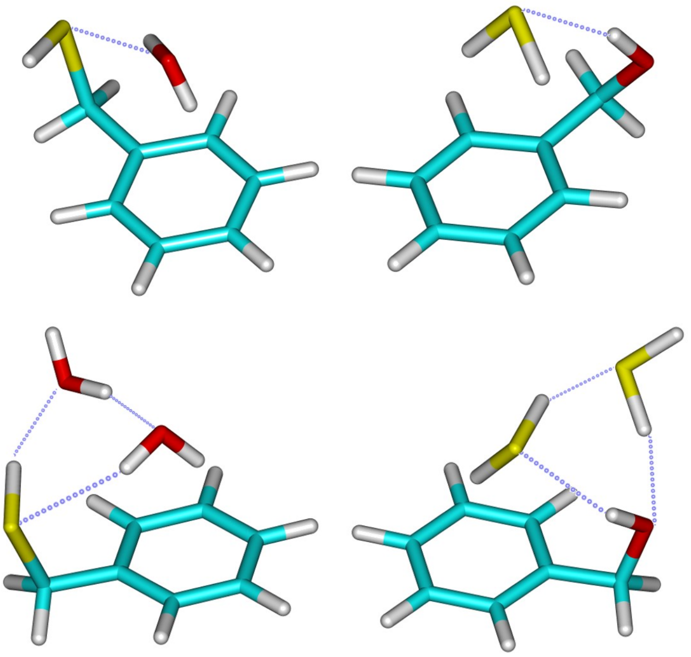
Hydrogen Bonding Competition Between Water and Hydrogen Sulfide: MW Spectroscopy of Microsolvation of Benzyl Alcohol and Benzyl Mercaptan

R. T. Saragi[1], M. Juanes[1], R. Pinacho[2], M. Jaraíz[2], A. Lesarri[1]*

[1]University of Valladolid, Departamento de Química , [2]University of Valladolid, Departamento de Electrón

We observed several intermolecular complexes involving H_2O or H_2S with benzyl alcohol and benzyl mercaptan, analysing the microsolvation and hydrogen bonding competition between the two hydrides. The clusters were generated in a jet-cooled expansion and characterized using chirped-pulse Fourier-transform microwave spectroscopy in the region 2-8 GHz. In the benzyl alcohol monosolvates, the aromatic alcohol acts as a proton donor, in opposition to the benzyl mercaptan dimers where the thiol group acts as a proton acceptor. For the bisolvated trimers, we observed two H_2O or H_2S molecules binding to benzyl alcohol and two water molecules attaching to benzyl mercaptan, always stabilized by cooperative hydrogen bonding. The clusters additionally involved secondary interactions between the solvents and the π ring system. Detailed information on the noncovalent interactions and molecular structures results from the combination of rotational data and DFT and ab initio molecular orbital calculations.



THE CHEMISTRY OF PAH-$(H_2O)_n$ CLUSTERS: A ROTATIONAL SPECTROSCOPY STUDY OF AZULENE DIMER AND ITS INTERACTIONS WITH WATER

S. Saxena[1], M. E. Sanz[1]*

[1]Department of Chemistry, King’s College London, London SE1 1DB, United Kingdom

The noncovalent interactions present in aromatic complexes are of great relevance in fields ranging from astrochemistry to biomolecular recognition. Polycyclic aromatic hydrocarbons (PAHs) are the most abundant class of molecules present in the carbonaceous materials and the building blocks of interstellar dust grains. Azulene is one of the smallest PAHs with a dipole moment. Here we present the results on the investigation of azulene dimer and its interactions with water molecules using chirped-pulse Fourier transform microwave spectroscopy. A stacked, rotated configuration of azulene dimer has been experimentally observed in the spectrum where dispersion forces between the π electronic densities are predominant. In both $(\text{azulene})_2\cdots H_2O$ and $(\text{azulene})_2\cdots(H_2O)_2$ complexes, water molecules establish O-H···π hydrogen bonds with one azulene and forms secondary C-H···O interactions with the other azulene. The azulene rings also interact with each other through dispersion interactions. Experimental observations are compared with predictions by theoretical methods to evaluate the performance of the latter. Our results contribute to understanding aggregation and microsolvation processes of PAHs in the gas phase.

The N_2-water complexes studied in the 1 OD and 2 OH stretching regions

R. Glorieux[1], C. Lauzin[1], A. Bogomolov[2], A. J. Barclay[3], M. Herman[4], N. Moazzen-Ahmadi[3]

[1]Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Chemin du cyclotron, 2 1348 Louvain-la-Neuve, Belgium, [2]Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk, Russia, [3]Department of Physics and Astronomy, University of Calgary, 2500 University Drive North West, Calagry, Alberta T2N 1N4, Canada, [4]Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES), Faculté des Sciences, Université libre de Bruxelles (ULB), 50 ave. F-D Roosevelt, B-1050, Brussels, Belgium

The rovibrational spectra of N_2-D_2O, N_2-DOH and N_2-H_2O were measured around the 1 OD and 2 OH stretching regions. A combination band involving the intermolecular in-plane N_2 bending vibration was also observed in each spectral region. The bands observed around the 1 OD stretching region were measured at the University of Calgary using a pulsed-slit supersonic jet expansion and a mid-infrared tunable optical parametric oscillator. The N_2-H_2O spectra were measured at the UCLouvain using the FANTASIO+ setup [1,2]. The spectra were analyzed by considering the feasible tunneling motions and fit to a series of independent asymmetric rotors. The rotational constants of the four tunneling components of N_2-D_2O and N_2-H_2O were retrieved for the excited vibrational states. The tunneling splittings are discussed as a function of the vibrational state and the nature of the isotopologues.

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The conformational landscape of 2-Pinen-10-ol and its water complex

E. M. Neeman[1], N. Osseiran [1], T. R. Huet[1]

[1]Université de Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, Lille 59000, France

Biogenic volatile organic compounds (BVOCs) are emitted in large quantities into the earth atmosphere and play a major role in the atmospheric chemistry. Monoterpenes ($C_{10}H_{16}$) represent 11% of the global BVOCs emission.[1] Our group recently investigated the hydration of endo-fenchol in the gas phase a combination of Fourier transform microwave spectroscopy (FP-FTMW) coupled to a supersonic jet expansion and theoretical calculations. One conformer was observed and the role of the hydrogen bond in the stabilization of the observed structure was described.[2] To go one step further, we considered 2-Pinen-10-ol. The conformational landscape of the monoterpene alcohol 2-Pinen-10-ol (6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-methanol) has been studied recently, and three conformers were observed and assigned to calculated structures.[3] In the present work, the hydrogen bonding linking 2-Pinen-10-ol to water has been investigated. A similar approach combining quantum chemical calculations with FP-FTMW spectroscopy was employed.[4,5] Five structures have been calculated below 8 kJ. Only one monohydrated conformer has been observed and assigned to a calculated structure. In addition the conformational landscape of the monomer has been reinvestigated. Geometry optimizations and harmonic vibrational frequency calculations were performed in order to characterize the equilibrium structure of conformers. Among the nine predicted structures, four have been observed, analyzed and identified. In addition, Deuteration of hydroxyl groups (OD) have been also studied which led to the determination of r_s geometry and confirm the identity of the observed species.[6]

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Dual role of π electrons in furan mapped on the furan–CF_3Cl complex studied by rotational spectroscopy combined with theoretical calculations

Y. Zheng[1], Q. Yang[2], Y. W. Cheng[1], M. Z. Jiang[2], J. Bloino[2]*, Q. Gou[1]*

[1]Department of Chemistry and Chemical Engineering, [2]SMART laboratory

style="text-align: justify;">The very recent rotational study on CF_3Cl–CO_2 reveals that the Cl “equatorial belt” in CF_3Cl can be activated by the π-hole region on CO_2, forming a C•••Cl tetrel bond.[1] On the other hand, the aromatic π* antibonding orbital can be activated by the partner with high electronegativity, like CF_4, as found in the rotational study of the benzaldehyde–CF_4 complex.[2] In this work, through the combination of rotational spectroscopy and quantum chemical calculations, we studied the structures and noncovalent interactions between furan and CF_3Cl. Two isomers were observed in the pulsed jet. For the most stable one, the Cl “equatorial belt” in CF_3Cl prefers to link with the delocalized aromatic π* antibonding orbital in furan. The second observed isomer, instead, is stabilized by the Cl•••π halogen bond formed between the Cl *σ*-hole of CF_3Cl and C=C-C=C diebe structure of furan. To support experiment, calculations beyond the harmonic-oscillator approximation were carried out, which allow the inclusion of vibrational averages in the rotational constants. Thanks to the availability of high-resolution reference experimental data for the observed isomers, a detailed study of the quality of electronic structure calculations based on DFT functionals and the treatment of large amplitude motions related to the intermolecular vibrations in complexes was carried out. This work has paved the way into devising better control mechanisms to reduce the risk of error compensations and identify possible pitfalls in anharmonic calculations based on perturbed approaches, and helped design more reliable computational protocols to support the experimental analysis for new and floppy systems. In particular, the validity of hybrid schemes combining harmonic force field and structural parameters at a higher level of theory with anharmonic constants built at a lower level has been assessed.

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Gas-phase structure of borneol and isoborneol monomers and their microsolvated complexes.

P. Pinacho[1], M. M. Quesada-Moreno[2], M. Schnell[1,3]*

[1] Deutsches Elektronen-Synchrotron (DESY), [2]Departamento de Química Inorgánica, Universidad de Granada, [3]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel (CAU)

The Borneo camphor molecule ($C_{10}H_{18}O$) is a naturally occurring monoterpene present in many essential oils, with applications in medicine, food or perfume industry. Its structure is similar to that of camphor with a hydroxyl group instead of a ketone, and the different disposition of the OH group gives rise to two isomers, borneol and isoborneol. The microwave spectra of borneol, isoborneol and their microsolvated complexes with two of the most common solvents, water and DMSO, were generated in a supersonic expansion and characterized using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the 2-8 GHz frequency range. The search for experimental species was guided by quantum-chemical calculations, which also helped with the elucidation of the structures and the interaction points between the molecules. For both borneol and isoborneol monomers, three low energy forms are predicted, from which only one was experimentally identified in the gas phase. This could be due to relaxation processes coming from collisions with the carrier gas.

In the microwave spectra of both monomers the lowest energy forms for the 1:1 borneol-water and 1:1 isoborneol-water complexes were also found due to the ubiquity of water. In both cases, the complexes are stabilized by a hydrogen bond in which the water molecule acts as a hydrogen bond donor and the OH group acts as a hydrogen bond acceptor. In the experiments with DMSO, the lowest energy conformations for the 1:1 borneol-DMSO and 1:1 isoborneol-DMSO complexes were detected. Those are also predicted to be stabilized by hydrogen bonds, however, in this case the OH group of borneol or isoborneol acts as a hydrogen bond donor, while the DMSO carbonyl group acts as a hydrogen bond acceptor.

Spectroscopy of large Amplitude Motions: from Interstellar Chemistry to Molecular Structures

I. Kleiner[1]

[1]Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS UMR7583, Université Paris-Est Créteil et Université de Paris

The topic of my talk will concern molecules containing large amplitude motions and in particular molecules with one or two methyl (CH_3) internal rotors. Internal rotors are present everywhere in our environment, and they are important indicators of the physico-chemical conditions which exist in it. They are also excellent “sensors” for molecular structure determinations.

The high resolution microwave, millimeter and infrared spectra of those molecules cannot be treated by traditional Hamiltonian methods [1]. One of the goals of our work is to develop theoretical methods and codes to calculate the energy levels, and then to fit the observed line positions for this type of molecules. Following this strategy, we can provide reliable predictions of line positions and intensities for astrophysical molecules containing one internal rotor CH_3, such as methanol CH_3OH, methyl formate $HCOOCH_3$, acetic acid CH_3COOH, acetaldehyde CH_3CHO, acetamide CH_3CONH_2 or two-top molecules such as the methyl acetate molecule CH_3-O-C(=O)-CH_3 [2]. The major new facilities, i.e. the Atacama Large Millimeter Array (ALMA), in Chili, have opened the sub-millimeter region for astronomical observations. Molecules which undergo internal rotation of a methyl group present thousands of lines in this spectral range and therefore their spectra are particularly important to model. Several internal rotors of astrophysical interest will be presented as well as the latest results obtained with a newly written code to deal with one Large-Amplitude Rotatory Motion and one Large-Amplitude Oscillatory Motion such as in the excited states of methyl amine [3].

Another goal of our work is to acquire knowledge on structural properties of small organic molecules or biomimetic molecules. Fourier transform or “chirped pulse” microwave spectroscopy in the gas phase coupled with high level quantum chemical calculations has led to precise and detailed determinations of molecular structures for lowest energy conformers of a number of molecules. In this talk, I will show results for molecules with internal rotors, which are prototype for odorant molecules like linalool, an acyclic mono-terpene present in many plants and emitted in the earth atmosphere, important phytohormones produced by plants such as methyl jasmonate or bee pheromones like heptan-2-one. Recent results obtained on methyl and dimethyl derivatives of five or six-membered nitrogen aromatic rings of biological interest will be also presented.

This work has been supported by French National programs PCMI (Programme National de Physique Chimie du Milieu Interstellaire) and LEFE (Les Enveloppes Fluides et l'Environnement) of CNRS.

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A doorway to vibrational resonance and other benchmarkable quantities in hydrate clusters

M. A. Suhm[1]

[1]University of Göttingen, Institute of Physical Chemistry, Tammannstr. 6, 37077 Göttingen, Germany

Monohydrate complexes of organic molecules at low temperature in vacuum isolation are natural benchmark systems for the ability of electronic structure theory and vibrational models to describe (micro-)solvation. The talk will focus on the OH stretching fundamentals and discuss a recently discovered anharmonic resonance which is systematically observed in ketone monohydrates and perhaps other hydrate clusters, whenever the OH fundamental falls in a narrow window slightly above 3500 cm^{-1}. It is suggested to be of 1-3 Darling-Dennison character, involving the water bend overtone and a water libration (b2lib) [1]. This study was made possible by a new gas recycling concept for jet FTIR spectroscopy [2], which allows to study costly isotopes and chemicals and to use expensive carrier gases.

The b2lib observation provides the starting point for a concerted effort to reliably model water OH stretching modes, when hydrogen-bonded to different organic molecules, whether resonance perturbed or not. In the HyDRA blind challenge starting this year [3], theory groups are invited to suggest all kinds of ab-initio, density functional, semiempirical, empirical, machine learning or other approaches to predict water OH stretching wavenumbers for a test set of 1:1 organic hydrate complexes. For this, they can build on an initial training set [4] and the spectroscopy community is invited to extend this training set into a growing data base. Progress will be discussed at an International Bunsen Discussion Meeting in Göttingen next March [5]. After completion of this initial, rather focussed HyDRA blind challenge next year, it is hoped that further research groups will extend the effort to wider ranges of hydrogen bond strength, to other spectroscopic observables, and to other perspectives or solvents. In the end, the most consistent and most economic tools to assist experimental spectroscopy in predicting key observables for hydrogen-bonded clusters might be identified for the benefit of our community.

If time permits, systematic benchmarking for the vibrational spectroscopy of alcohols [6] and vicinal diols will also be discussed.

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Big Game Hunting: Tools and Techniques for Identifying Large Molecules in Space

B. A. McGuire[1,2]

[1]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA USA, [2]National Radio Astronomy Observatory, Charlottesville, VA USA

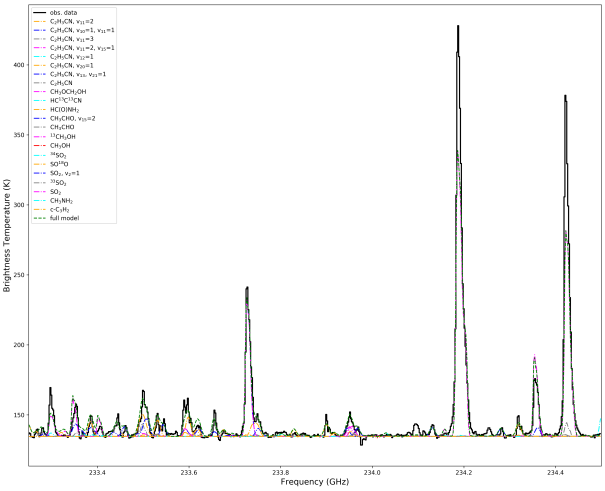
The last few years have seen an explosion in discoveries of new carbon molecules at centimeter wavelengths, particularly using observations from the Green Bank Telescope and the Yebes 40-m telescope. These have included numerous long-sought precursor species, ringed species, and the first detections if individual polycyclic aromatic hydrocarbons since their attribution as the carriers of the unidentified infrared emission bands in the mid 1980s. In this talk, I will highlight just what makes the centimeter-wavelength regime so good for detecting large cold carbon molecules, highlight a number of the recent remarkable discoveries in this area, and discuss the implications and paths forward.

Recent progress and challenges in analyzing complex astrophysical spectra

P. Schilke[1], T. Möller[1], Á. Sánchez-Monge[1]

[1]I. Physikalisches Institut, Universität zu Köln

The sensitivity of recent (Herschel/HIFI, ALMA, JVLA) and future (SKA, ngVLA) astrophysical instruments has brought on a plethora of observations of very rich spectra in a variety of object classes: stellar envelopes, hot cores, hot corinos, but also shocked regions. Extracting all the information in a timely manner has been a challenge, particularly if one goes from more traditional single spectra to spectral cubes.



We identify the following main challenges:

- Line blending: if one wants to identify and characterize single species, one cannot do that in isolation, but has to identify all species to be sure one understands the overlaps and does not misidentify species,
- Excitation conditions: line blending can also severely hamper the ability to determine source parameters such as temperatures, if line blendings are not identified or corrected for,
- Non-LTE conditions: most line fits are done under the LTE assumption, partly because it is justified in many cases because of high densities, partly out of necessity, since collision rates for many species do not exist, or are restricted to a rather small basis set and/or narrow temperature range,
- Source structure: most fitting methods assume one or at best a few components that may or may not interact, this often is a rather crude approximation of the complex density and temperature structure of real sources,
- Molecular Line Catalogs: although this is left as the last point of the list, their incompleteness often is the dominant source of uncertainty in fitting. This has two aspects: looking for new species with (in most cases) weak lines requires a good understanding of all the other lines, and excitation studies, particularly close to the exciting sources, require the knowledge of highly excited lines, often of vibrationally excited levels, including of isotopologues, that often doe not exist.

While the first four points can be dealt with to some degree with new and better modeling approaches (e.g. XCLASS https://xclass.astro.uni-koeln.de/) and implementing novel concepts drawn from Machine Learning methods (although they are ultimately limited by the fact that constraining the true 3-d structure from observations will not always be possible), the last point requires more and better molecular catalogue entries, probably also requiring new methods of data acquisition and analysis.

Rotational Action Spectroscopy in Ion Traps

O. Asvany[1]

[1]I. Physikalisches Institut, Universität zu Köln

Rotational action spectroscopy is an experimental method in which rotational spectra of molecules are recorded by action spectroscopy. Action spectroscopy means that the spectrum is recorded not by detecting the absorption of light by the molecules, but by the action of the light on the molecules, e.g., photon-induced destruction of a chemical bond, a photon-triggered reaction, or photodetachment of an electron. Typically, such experiments are performed on molecular ions, which can be well controlled and mass-selected by established guiding and storage techniques. Though coming with many advantages, the application of action schemes to rotational spectroscopy was hampered for a long time by the small energy content of a corresponding photon. Therefore, the first rotational action spectroscopic methods emerged only about one decade ago. Today, there exists a toolbox full of different rotational action spectroscopic schemes. This talk summarizes the different rotational action spectroscopic approaches and gives an outlook on the application of these schemes to exotic hydrogen-helium complexes of the form $H_nHe_m{}^+$.

Deciphering the infrared emission of astro-PAHs: the interplay between laboratory experiments, quantum chemistry and modelling

C. Joblin[1], G. Mulas[1,3], S. Chakraborty[1], K. Demyk[1], D. Toublanc[1], M. Rapacioli[2], A. Simon[2], O. Berné[1]

[1]Institut de Recherche en Astrophysique et Planétologie (IRAP), Université Toulouse 3, CNRS, CNES, France, [2]Laboratoire de Chimie et Physique Quantiques (LCPQ), Université Toulouse 3, CNRS, France, [3]INAF, Osservatorio Astronomico di Cagliari, Italy

The aromatic infrared bands (AIBs) are major dust emission features that Astronomers aim to use to trace variations in the physical and chemical conditions in regions of star formation from the small scales of protoplanetary disks to the large scales of galaxies. The AIBs also carry information on the chemical complexity of their emitters, which mainly consist of polycyclic aromatic hydrocarbons (PAHs) that are heated by the absorption of ultraviolet (UV) photons. A detailed analysis of the AIB spectra requires taking into account molecular diversity together with excitation conditions. In heated molecules, vibrational coupling (anharmonicity) plays a major role, affecting the band positions and widths [1] and leading to a number of new bands such as combination/difference bands and overtones. Disentangling temperature effects from chemical complexity requires a detailed comparison of the observed spectra with synthetic spectra that model the emission of a given PAH molecule in a given UV-visible astrophysical radiation field.

The necessary molecular data ingredients for the model are the UV-visible photoabsorption spectrum, the vibrational modes and IR absorption cross-sections, and in principle rotational constants although rotational broadening can be neglected in most cases except for low frequency bands [2]. These data have been and are still being gathered in several dedicated databases [3,4]. However, anharmonic effects are poorly covered and need to be included to generate the simulated IR spectra that can be compared to the astronomical AIB spectra. Obtaining empirical anharmonic parameters that describe the evolution of the band positions and widths with temperature has been the focus of our recent research both using experimental methods [5] and quantum chemistry calculations [6]. An emission code is also being developed in order to build a simulator for a fast calculation of the emission of a given PAH in a given radiation field. The simulator will provide a library of synthetic AIB spectra (the LAIBrary project) based on theoretical and experimental molecular data, at the accuracy and sensitivity level required to match coming James Webb Space Telescope (JWST) observations such as the Early Release Science programme “Radiative feedback from massive stars” (http://www.jwst-ism.org).

Support from CNES (ID 5830) and the Nanocosmos ERC Synergy project (G.A. 610256) is acknowledged.

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Program, Thursday, September 2, 2021

Contributed Talks (K)

	Environment (KA) Chair: Clément Lauzin, UCLouvain, Belgium	**Processes (KB)** Chair: Roman Motiyenko, Université de Lille, France	**Techniques (KC)** Chair: Melanie Schnell, DESY, Hamburg, Germany
12.00	***Larisa Troitsyna***, Université Bourgogne Franche-Comté «Room temperature oxygen- and air-broadening coefficients for the v_6 band of methyl iodide»	***Pascal Heim***, University of Technology Graz «Ultrafast Nonadabatic Dynamics of Nearly Degenerated Rydberg States in Acetone»	***Thomas Hearne***, Université Paris-Saclay «New Spectroscopic methods for THz synchrotron beamlines»
12.15	***Tatyana A Odintsova***, RAS, Nizhniy Novgorod, Russia «On the origin of the water vapor continuum absorption within H_2O rotational band»	***Matthew H. Rayment***, University College London «Slow-decay processes of long-lived Rydberg states of nitric oxide»	***Charles R Markus***, The California Institute of Technology «Cavity-Enhanced Direct Frequency Comb Spectroscopy in the CH Stretching Region with Interband Cascade Lasers»
12.30	***Jolanta Domysławska***, Nicolaus Copernicus University «Direct observation of the line mixing in the oxygen B ban»	***Nicolas Hölsch***, ETH Zurich «Ionization Energies of Para-H_2 from Zero-Quantum-Defects Positions»	***Daniel Lisak***, Nicolaus Copernicus University «Dual-comb cavity ring-down spectroscopy»
12.45	***Amal Farji***, University of Tunis/ Université Libre de Bruxelles «Air-induced collisional parameters in the n_3 band of methane»	***Kenneth J. Koziol***, RWTH Aachen University «Quenching the Effects of Proton Tunnelling and Methyl Internal Rotations of Dimethylamine by Water Addition»	***Katarzyna Bielska***, Nicolaus Copernicus University «Cavity mode-dispersion spectroscopy applied in saturation conditions»
13.00	***Noureddin Osseiran***, Université de Lille «Complexation of atmospheric BVOCs in the gas phase: Theoretical and FP-FTMW study»	***Thibault Bertin***, Université Libre de Bruxelles «CO_2 collision-induced line parameters in the v_3 band of CH_4»	***Guillaume Dhont***, Université du Littoral Côte d'Opale «Molecules probed with a slow chirped-pulse excitation: analytical model of the free-induction-decay signal»
13.15	***Aleksandra Koroleva***, Université Grenoble Alpes, CNRS «Foreign water vapor continuum in the far infrared (50-500 cm^{-1})»	***Jordan Claus***, Université de Lille, CNRS, PhLAM «The hydration of polycyclic aromatic compounds: the case of 1-naphthaldehyde»	***Soumaya Bezzaouia***, Faculty of Sciences of Tunis/University of Tunis El Manar «Potential energies and electronic dipole transition moments of confined hydrogen in spheroidal boxes»

13.30 Break

Invited Lectures (L)
Chair: Jonathan Tennyson, University College London, UK

14.00 ***Clara Sousa-Silva***, Harvard-Smithsonian Center for Astrophysics
«Finding an Alien Biosphere with Computational Chemistry»

14.45 ***Anne Amy-Klein***, Université Sorbonne Paris Nord, CNRS
«High-precision molecular spectroscopy referenced to frequency standards at the 10^{-14} level»

15.30 Break

16.00 **Poster Session 1**
Watch the short video presentations
Meet the poster presenters on the interactive platform MeetAnyway

17.30 End of day 5

Room temperature oxygen- and air-broadening coefficients for the ν_6 band of methyl iodide

L. Troitsyna[1], J. Buldyreva[1], A. Dudaryonok[2], N. Lavrentieva[2], N. Filippov[3]

[1]Institut UTINAM UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 route de Gray, 25030 Besançon cedex, France, [2]Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS,1 Akademician Zuev Sq., 634055 Tomsk, Russia, [3]St Petersburg State University, 7/9 Universitetskaya emb., 199034 St Petersburg, Russia

Methyl iodide is the chief iodine-containing atmospheric constituent and, as it is naturally produced in the oceans, is believed to play a role in the formation of marine clouds, that influence the terrestrial radiative budget by scattering the incoming radiation [1]. Since sounding from satellites is an efficient way to study the global distribution of a trace gas, the bands that fall into the atmospheric transparency windows, e.g., the ν_6 band of methyl iodide, and their spectroscopic characteristics are of particular interest for atmospheric applications.

The goal of the present work is to provide theoretical estimates of line-broadening coefficients of CH_3I-O_2 and CH_3I-air in a wide range of rotational quantum numbers ($0 \leq J \leq 70$ and $K \leq 20$) typically required by databases [2-3]. For these purposes a semi-classical (Robert-Bonamy approach with classically calculated “exact” trajectories) [4] and a semi-empirical (analytical expression of the Anderson theory fitted on some experimental values via an empirical correction factor) [5] methods are utilized. The comparison of these results with a set of experimental data [6] for the case of CH_3I-O_2 and with two sets of experimental data [6, 7] for CH_3I-air proves that both methods provide good estimates of line-broadening.

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On the origin of the water vapor continuum absorption within H_2O rotational band

T. A. Odintsova[1], A. O. Koroleva[1,4], A. A. Simonova[2], O. Pirali[3,5], A. Campargue[4], I. V. Ptashnik[2], M. Tretyakov[1]

[1]Institute of Applied Physics of RAS, Nizhniy Novgorod, Russia, [2]V.E. Zuev Institute of Atmospheric Optics SB RAS, Tomsk, Russia, [3]Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, Orsay, France, [4]Univ. Grenoble Alpes, CNRS, LIPhy, Grenoble, France , [5]SOLEIL Synchrotron, L'Orme des Merisiers, Saint-Aubin, Gif-Sur-Yvette, France

It is commonly accepted that the water vapor continuum absorption originates from collisional interaction of H_2O molecules, namely from wings of resonance lines and water dimer (stable and metastable) absorption. However, the relative contribution of each of these mechanisms has to be clarified.

The water vapor continuum absorption has been investigated in the pure rotational band of H_2O molecule. Series of measurements using Fourier Transform spectrometer on SOLEIL synchrotron facility were carried out to record water vapor absorption spectra in a broad frequency region (15-700 cm^{-1}) under various thermodynamic conditions (1-15 mbar, 296-326 K) [2-4]. On the one hand, the continuum absorption in this spectral region is of particular importance since it covers the maximum of the Earth thermal emission. On the other hand, it is advantageous for styding of nature of the water vapor continuum because only this spectral range is supported by *ab initio* calculations of the water dimer spectrum [1].

The retrieved self-continuum cross-sections are found to be in a good agreement with literature values available in the lower and upper parts of the studied frequency region [5-7]. All experimental data indicate the need for correction of the empirical continuum model MT_CKD [8] widely used for atmospheric applications.

A comparative analysis of the retrieved data on the continuum absorption with the results of *ab initio* calculations of the water dimer spectrum [1] provides *(i)* a confirmation of the dominant role of water dimers in formation of the water vapor continuum in the mm-submm range and (*ii*) evidence of a significant contribution of other mechanisms of continuum formation (wings of resonance lines and metastable dimers) in the higher-frequency far-IR region.

The study is partly supported by RFBR-CNRS project 18-55-16006.

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Direct observation of the line mixing in the oxygen B band

J. Domysławska[1], S. Wójtewicz[1], K. Bielska[1], S. Bilicki[1], R. Ciuryło[1], D. Lisak[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland

We present the results of CRDS investigation of two pairs of overlapping transitions in the oxygen B-band head.

Measurements were performed with frequency-stabilized cavity ring-down spectrometer (FS-CRDS) referenced to an optical frequency comb. We exploited the new setup of the spectrometer in dual-polarization configuration which allows for the probe beam to be switched and tuned independently from the PDH lock beam, similarly as described in Ref. [1]. The R19R19, R21R21, R19Q20, and R21Q22 lines were measured in the pressure range up to 32 Torr with actively stabilized temperature to 296 K. Recorded spectra were analyzed using the multispectrum fitting technique in order to reduce the numerical correlations between fitted line-shape parameters [2, 3]. The line-shape models fitted to the spectra included speed dependence (speed-dependent Voigt profile, SDVP), speed dependence and Dicke narrowing (speed-dependent Nelkin-Ghatak profile, SDNGP) and line mixing (SDVP + LM, SDNGP + LM) [4]. Line positions, line intensities, pressure coefficients for broadening, shifting and narrowing were determined with the quality-of-the-fit QF (the ratio of the peak absorption signal to the standard deviation of the fit residuals [5]) parameter exceeding 22000 for the best fits. Although the pressure was as low as 0.04 of atm we were able to determine the first-order O_2-O_2 line mixing coefficients and explain some questions concerning line shifts and speed-dependent parameters [6]. Incorporation of the line mixing in the oxygen B band modeling is also crucial in the collision-induced absorption (CIA) determination [7]. Results for LM parameters were compared with available calculated data [7].

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Parallel Session: Environment, Contributed Talk (15min) **KA4**

Air-induced collisional parameters in the n_3 band of methane

A. FARJI[1,2], J. Vander Auwera[2]*, H. AROUI[1]*

[1]Laboratoire de Spectroscopie et Dynamique Moléculaire, Université de Tunis, Ecole Nationale Supérieure d'Ingénieurs de Tunis, Tunisia, [2]SQUARES, C.P. 160/09, Université Libre de Bruxelles

style="text-align: justify;">Methane is an important constituent of the atmosphere of the Earth and outer planets of the solar system [1]. Precise and detailed knowledge of spectroscopic line parameters of methane is crucial to measure its concentration in these atmospheres using remote sensing techniques.

In this work, high-resolution spectra of pure and air-broadened methane have been recorded in the 2600 – 3200 cm^{-1} spectral range at a resolution of 0.006 cm^{-1} (maximum optical path difference of 150 cm) with a Bruker IFS125 HR Fourier transform spectrometer available in Brussels. All the spectra were obtained using high purity natural samples of CH_4 and mixtures of the same natural CH_4 with dry air. The experiments were performed at an average temperature of 296 K, with an absorption path length of 19.7 cm and pressures ranging from 0.3 to 678 Torr.

We were able to fit the full range of pressures with a Rautian–Sobel'Man line shape model, which takes into account the Dicke narrowing effect, with Rosenkranz line mixing. For the analysis, a multi-spectrum non-linear least squares fitting software was employed in which all the spectra were fitted simultaneously. Spectral line shape parameters (air broadened widths, shifts, Dicke narrowing and first order line mixing coefficients) have been determined for 166 lines belonging to J" manifolds of the P (J" = 2-11), Q (J" = 1-12) and R (J" = 0-11) branches of the n_3 band of $^{12}CH_4$ near 3.3µm.

Variations of the measured parameters with tetrahedral symmetry species, rotational quantum numbers and ranking indexes of the lower levels of the studied transitions, and comparisons with previous works will be presented and discussed.

Keywords: methane, n_3 band, High Resolution Infrared Spectroscopy, air broadening and shift coefficients, Dicke-narrowing, line-mixing parameters.

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Complexation of atmospheric BVOCs in the gas phase: Theoretical and FP-FTMW study

N. Osseiran [1], E. M. Neeman[1], M. Goubet[1], P. Dréan [1], T. R. Huet[1]

[1]Université de Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, Lille 59000, France

Biogenic volatile organic compounds (BVOCs) are emitted into the atmosphere naturally mainly via vegetation. Among these are monoterpenes ($C_{10}H_{16}$) and terpenoids (oxygen-containing terpenes), which are of atmospheric interest. These molecules can be oxidized by OH, O_3 and NO_x resulting in several oxidation and degradation products that alter numerous physical and chemical processes in the atmosphere. They can also form Van der Waals complexes and/or hydrogen-bonded complexes with water or other molecules present in the atmosphere. Within this context, many BVOCs along with their hydration complexes have been characterized in our group, with Fourier transform microwave spectroscopy (FTMW) employing Fabry-Perot spectrometers operating within the 2-20 GHz range.[1,2] A new approach will be presented here, which combines theoretical ab initio and DFT calculations with pure rotational spectroscopy in the microwave domain to characterize complexes of terpenoids with sulfur containing species instead of water. Most recent results will be presented, including a discussion on H-bonding from sulfur containing species, on experimentally observed systems.[3]

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Foreign water vapor continuum in the far infrared (50-500 cm^{-1})

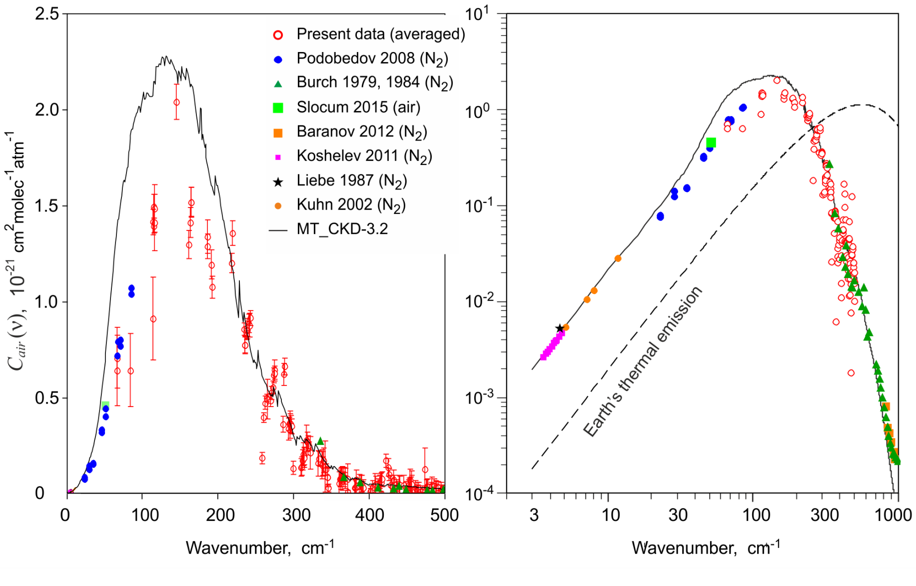
A. Koroleva[1,3], T. Odintsova[1], M. Tretyakov[1], O. Pirali[2,4], A. Campargue[3]

[1]Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia, [2]Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, Orsay, France, [3]Univ. Grenoble Alpes, CNRS, LIPhy, Grenoble, France , [4]SOLEIL Synchrotron, L'Orme des Merisiers, Saint-Aubin, Gif-Sur-Yvette, France

The foreign-continuum absorption of water vapour diluted in nitrogen, oxygen and air has been measured in the range of H_2O pure rotational band (50-500 cm^{-1}). This work is a continuation of our works [1-3], where the self-continuum component was determined in the same region. Spectra recordings were performed at room temperature with a Fourier transform spectrometer associated to a 151-m multipass gas cell located at the AILES beamline of the SOLEIL synchrotron. The HITRAN2016 line list and self-continuum data from [1] were used to extract the foreign-continuum from the experimental spectra. Tests of the baseline stability which is crucial for the continuum determination, were performed. The spectra were recorded for a series of pressure values. The expected linear pressure dependences of the foreign-continuum were checked for all gas mixtures under consideration. Consistency between retrieved H_2O-N_2, H_2O-O_2, and H_2O-air foreign-continuum cross-sections was shown.

The study includes the first laboratory measurements in the wide 90-330 cm^{-1} spectral interval. Retrieved foreign-continuum cross-sections are found in good agreement with literature values available in the lower and upper parts of the studied frequency range (see figure). The reported results validate the MT_CKD [4], widely implemented in radiation transfer codes used for the atmosphere and underlying surface remote sensing, even if some overestimation of the MT_CKD values is noted in the centre of the band where experimental data were absent.

This work is partially supported by RFBR project 18-55-16006.



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Ultrafast Nonadabatic Dynamics of Nearly Degenerated Rydberg States in Acetone

P. Heim[1], S. Mai[2], B. Thaler[1], S. Cesnik[1], D. Avagliano[2], D. Bella-Velidou[2], W. E. Ernst[1], M. Koch[1]*, L. González[2]*

[1]University of Technology Graz, Institute of Experimental Physics, [2]University of Vienna, Institut of Theoretical Chemistry

Photoexciting molecules introduces complex relaxation dynamics which can be studied by time-resolved photoelectron spectroscopy. Hereby, broadband laser sources are used to achieve the desired time resolution. However, if the bandwidth of the laser pulses is broader than the energy spacing between the involved states two problems occur: (i) Exciting the molecule into one specific initial state is not possible. (ii) Simple parallel or sequential decay models are not applicable due to the complex coupling of the different states, and more complex models are underdetermined. Theoretical calculations, in contrast, are not limited by these problems as they can arbitrarily define an initial population and are able to track the transient behavior directly. However, the retrieved dynamics require experimental verification to achieve reliability.

In this study we present a combined approach of time-resolved photoelectron spectroscopy and surface-hopping simulations to investigate the dynamics of electronically excited acetone molecules [1]. The nearly degenerated n3p Rydberg states are ideal to benchmark this approach because (i) the three n3p Rydberg states are energetically well separated to other states, (ii) the kinetic energy of photoelectrons which are created by ionization into the ionic Rydberg ground state show no energy dependence of the vibrational state (because the involved energy curves are parallel) and (iii) the n3p_y state has an avoided crossing with a ππ* valence state which differentiates the n3p_y from n3p_x and n3p_z, introducing more variety in the problem.

The influence of the excitation energy on the relaxation times and ultimately on the coupling between the different involved states can be studied by fitting decay associated spectra to the measured spectrograms. However, the decay associated spectra only show one effective time constant per involved state. To get insight into the intrinsic dynamics surface hopping simulations with the SHARC [2] program package in combination with a linear vibronic coupling model were performed. The reliability of the simulations can be confirmed by computing the effective time constants from the coupling strength between the states and comparing them to the experimental values. The good agreement allows interpretation of the computational results: (i) The coupling from an energetically higher to a lower state is stronger than vice versa because of the larger accessible phase space in the lower state. (ii) The n3p_y state couples strongly to the ππ* valence state because of the avoided crossing. (iii) The coupling between n3p_x and n3p_z to the ππ* state is much weaker than to the n3p_y. Population of these states use the n3p_y as a doorway state in order to relax to the ground state. (iv) Increasing the excitation energy also increases the coupling strength. The good agreement of experiment and simulations provide a detailed understanding into the complex dynamics of the nearly degenerated n3p Rydberg states, which would not be possible by one method alone.

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Slow-decay processes of long-lived Rydberg states of nitric oxide

M. H. Rayment[1], S. D. Hogan[1]*

[1]Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom

High Rydberg states of small molecules play an important role in electron-ion recombination in laboratory, atmospheric, and astrophysical plasmas [1-3]. However, until recently laboratory studies of the slow decay dynamics of molecules in these excited states have not been possible [4,5]. Here we describe a unique, state-of-the-art cryogenically cooled chip-based Rydberg-Stark decelerator, and the use of this device to electrostatically trap nitric oxide (NO) molecules for the first time [6]. Trapping the molecules, prepared in long-lived Rydberg states using resonance-enhanced two-colour two-photon excitation from the X $^2\Pi_{1/2}$ ground state, for up to 1 ms enabled precise measurements of the excited state decay rates. These measurements were performed for molecules photoexcited to Rydberg states with principal quantum numbers, n, between 32 and 50, in Rydberg series converging to the $N^+ = 0$, 1, and 2 rotational states of the $v^+ = 0$ vibrational state of NO^+. For the range of Rydberg states studied, decay time constants of ~300 μs were observed. However, counterintuitively, these decay times decreased as the value of n was increased, and therefore did not follow the n-scaling rules typical of high Rydberg states. Additionally, for some particular values of n deviations from this trend were seen. These observations were interpreted, with the aid of numerical calculations of the energy-level structure and lifetimes of the Rydberg states, to arise as a result of weak rotational and vibrational channel interactions. The vibrational channel interactions, between Rydberg states in the $v^+ = 0$ vibrational series and nearby short-lived low-n states in the $v^+ = 1$ series, resulted in contributions to the total excited-state decay rates on the order of 1 kHz. Rotational channel interactions, within the $v^+ = 0$ series, were identified to specifically affect the decay time constants of some individual Rydberg states.

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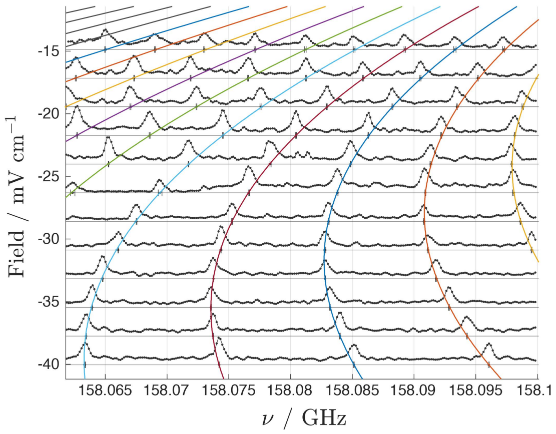
Ionization Energies of Para-H_2 from Zero-Quantum-Defects Positions

N. Hölsch[1], I. Doran[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich

From the precise measurement of the ionization energy of H_2 its dissociation energy can be determined [1], which serves as a benchmark quantity for QED calculations [2]. Additionally, measurements of ionization energies corresponding to higher rovibrational levels of the ion enable the determination of rovibrational intervals in H_2^+ [3]. These intervals can be calculated extremely precisely for one-electron systems, offering the prospect of improving the value of fundamental constants or particle properties such as the proton-to-electron mass ratio [4]. Until now, the most precise determinations of the ionization energies of molecular hydrogen have relied on the extrapolation of Rydberg series using multichannel quantum-defect theory (MQDT) [5]. These extrapolations are typically accurate to less than 500 kHz, currently representing the dominant source of uncertainty in the determinations of ionization energies. Additionally, autoionization lifetimes restrict mmW measurements to states below the lowest ionization threshold which renders accurate extrapolations to higher rovibrational levels of the ion difficult.



We present here a method to determine the binding energies of Rydberg states without having to resort to a Rydberg-series extrapolation. We carry out precision measurements of the linear Stark manifolds associated with near-degenerate high-*l* states by mmW spectroscopy in the presence of intentionally applied electric fields. Extrapolating the linear Stark manifold to zero field yields accurate values of the zero-quantum-defect positions, given by $-R_{H2}/n^2$ relative to the ionization thresholds. This circumvents the current bottlenecks and opens a route for order-of-magnitude improvements of the ionization energies in molecular hydrogen.

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Quenching the Effects of Proton Tunnelling and Methyl Internal Rotations of Dimethylamine by Water Addition

K. J. Koziol[1], W. Stahl[1,3], L. Nguyen[2]

[1]Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany, [2]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7853, Université Paris-Est Créteil, Université de Paris, 61 avenue du Général de Gaulle, F-94010 Créteil, France, [3]Posthumous abstract

The rotational spectra of dimethylamine[4] and its water complex have been investigated. In dimethylamine, the hydrogen atom of the amino group performs an inversion tunnelling motion, causing splittings of all *c*-type transitions into doublets with a separation of 2646.0 MHz[4]. The first microwave spectrum of dimethylamine has been recorded in 1968 using a Stark modulated spectrometer with a resolution of 25 kHz. The ^{14}N quadrupole hyperfine structure was reported to be resolved only for some transitions and the internal rotation splittings in the vibrational ground state could not be resolved.

In the present work, the spectra of dimethylamine were remeasured using two molecular jet Fourier transform microwave spectrometers operating from 2 to 40 GHz. The proton tunnelling was analysed, taking Coriolis interactions into account which cause splittings in the order of about 0.2 to 1.2 MHz for all *b*-type transitions. Furthermore, hyperfine splittings due to the quadrupole coupling of the ^{14}N nucleus were fully resolved. The quadrupole coupling constants X_{aa} and $X_{bb} - X_{cc}$ were determined with high accuracy and calculated well using Bailey's method[5]. The splittings into triplets in the order of 200 kHz, arising from internal rotations of two equivalent methyl groups, could be resolved. The addition of water to dimethylamine has deactivated the proton tunnelling inversion as well as decreased the torsional splittings below the resolution limit of 2 kHz.

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CO_2 collision-induced line parameters in the ν_3 band of CH_4

T. Bertin[1], J. Vander Auwera[1]*

[1]SQUARES, C.P. 160/09, Université Libre de Bruxelles, 50 avenue F.D. Roosevelt, 1050 Brussels, Belgium

Methane is present in the atmosphere of a large number of objects in the Solar system and beyond. Probing CH_4 in these environments using optical remote sensing relies on the availability of appropriate information characterizing its spectrum. The present work aims to provide the spectroscopic information required to describe the effects of pressure on the infrared spectrum of methane in CO_2 dominated atmospheres, to compensate for the scarcity of the information currently available [1-7]. High resolution Fourier transform spectra of methane diluted in carbon dioxide at total pressures up to 800 hPa have been recorded at 296.5 (5) K in the pentad region around 3.3 µm. Their analysis is being carried out using multi-spectrum fitting techniques [8] and a quadratic speed-dependent Rautian line shape model with line mixing. Results will be presented and discussed.

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The hydration of polycyclic aromatic compounds: the case of 1-naphthaldehyde

J. Claus[1], C. Bermudez[1], L. Margulès[1], M. Goubet[1]

[1]Univ. Lille, CNRS, UMR 8523-PhLAM, Physique des Laser Atomes et Molécules F-59000 Lille , France

Polycyclic aromatic hydrocarbons (PAHs) and their oxygenated products (oxi-PAH) are considered as important pollutants of the Earth's atmosphere since they are emitted by the combustion of fuels.[1] The study of their intermolecular interactions is essential to understand the formation of their aerosols. In this work, we have studied at molecular level the interactions present in the hydration of the oxi-PAH, 1-naphthaldehyde. This study has been performed using a supersonic jet Fourier transform microwave (FTMW) spectrometer in the 4-15 GHz range, with the support of theoretical calculations. The isolated 1-naphthaldehyde species could present two possible structures: *cis,* the most stable one, and *trans*.[2] Our calculations show that there are three low energy monohydrates predicted for each conformer, *cis* / *trans*, in a range of 1500 cm^{-1}. Experimentally, a single conformer has been observed in gas phase, corresponding to the most stable one. This species is stabilized by two intermolecular H-bonds between the water molecule and the aldehyde group of *cis*-1-naphthaldehyde, where the oxygen of the aldehyde acts as proton acceptor and the aldehyde hydrogen as proton donor.[3]

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New Spectroscopic methods for THz synchrotron beamlines

T. Hearne[1], M. Mammez[2], D. Mammez[2], M. Martin-Drumel[1], P. Roy[3], O. Pirali[1], S. Eliet[4], F. Hindle[2], G. Mouret[2], J. Lampin[4]*

[1]Institut des Sciences Moleculaires d'Orsay, [2]Laboratoire de Physico-Chimie de l'Atmosphère, [3] Synchrotron SOLEIL, [4]Institute of Electronics, Microelectronics and Nanotechnology

Synchrotron beamlines are extremely useful light sources across the electromagnetic spectrum for sensitive, broadband spectroscopy, in the far-IR or terahertz (1-10 THz) region which lacks bright, broadband laboratory sources. Far-IR synchrotron beamlines across the world are equipped with Fourier-transform infrared (FTIR) spectrometers. These instruments provide broadband spectra thanks to the powerful multiplex advantage of interferometry. However, they are also inherently limited in their maximum resolution, to around 20 MHz for the best available instruments. This resolution is in excess of an order of magnitude larger than typical THz molecular linewidths, and prevents the observation of many fine and hyperfine effects.

The goal of the HEROES (heterodyne receivers optimized for synchrotron sources) project is to unlock far-IR synchrotron sources for higher resolution spectroscopy, while simultaneously improving sensitivity and maintaining the broadband advantage of FTIR spectroscopy. Two new spectrometers are under development to achieve this goal. The first is an instrument based on the heterodyne mixing of the output of a QCL-pumped molecular laser with the far-IR continuum of the regular synchrotron radiation.[1] The second is a dual-comb spectrometer combining the THz frequency comb produced by the coherent synchrotron radiation mode of the synchrotron[2] with a comb produced from the incidence of a femtosecond laser onto a spiral antenna photomixer. The latest progresses on the development on these two spectrometers will be presented.

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Cavity-Enhanced Direct Frequency Comb Spectroscopy in the CH Stretching Region with Interband Cascade Lasers

C. R. Markus[1], T. L. Chen[1], L. A. Sterczewski[2,3], D. C. Ober[1], M. Bagheri[2], M. Okumura[1]

[1]The California Institute of Technology, [2]The Jet Propulsion Laboratory, [3]Wroclaw University of Science and Technology

Optical frequency combs provide the benefits of continuous-wave narrow-band lasers while maintaining broadband coverage. Being composed of many equally spaced frequency components, or comb teeth, allows for them to be efficiently coupled into enhancement cavities for trace gas detection. There has been a push to implement this in the mid-infrared in order to take advantage of strong fundamental vibrational bands. However, mid-infrared frequency combs based on non-linear optics are bulky, expensive, and technically challenging. Interband cascade lasers are semiconductor devices which have been demonstrated to be compact and efficient sources from 3-6 µm. They can also be designed to act as optical frequency combs, providing 1 THz of coverage in the CH stretching region. Although they lack the coverage of fiber based femtosecond lasers, their simplicity and portability opens new possibilities. We have investigated cavity-enhanced schemes with these devices, including Vernier spectroscopy which allows for the full comb spectrum to be measured in ~1 ms with comb-tooth resolution. We present these results and discuss possible applications for these novel devices.

Dual-comb cavity ring-down spectroscopy

D. Lisak[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziądzka 5, 87-100 Toruń, Poland.

Co-authors: D. Charczun[1], A. Nishiyama[1], T. Voumard[2], T. Wildi[2], G. Kowzan[1], V. Brasch[3], T. Herr[2], A. J. Fleisher[4], J. T. Hodges[4], R. Ciuryło[1], A. Cygan[1], P. Masłowski[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziądzka 5, 87-100 Toruń, Poland.
[2]Center for Free-Electron Laser Science (CFEL), German Electro-Synchrotron (DESY), Notkestr. 85, 22607 Hamburg, Germany.
[3]CSEM - Swiss Center for Electronics and Microtechnology, 2000 Neuchâtel, Switzerland.
[4]Optical Measurements Group, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899, U.S.A.

Cavity ring-down spectroscopy has become a standard method for many research fields involving light-matter interactions because of its simplicity, high resolution, sensitivity and accuracy. In the only broadband demonstration of this technique with an optical frequency comb [1], the intrinsic spectral resolution of the ring-down cavity was degraded by orders of magnitude to the level of traditional dispersive spectrographs. Here we present dual-comb cavity ring-down spectroscopy (DC-CRDS) [2], in which mode-resolved spectra of the sample are retrieved from the dynamic response of the cavity to modulation of the excitation field. Instead of comb-comb beating signal used in conventional dual-comb spectroscopy [3], we exploit the beating between parallel optical cavity ring-down signals and a local oscillator comb. The absorption and dispersion spectra are retrieved in the frequency domain from the widths and positions of the Fourier-transformed decaying cavity modes [4,5]. We demonstrate two variants of the scheme based on excitation that is either coherently driven or incoherently driven. The former approach enables fast spectrum acquisition with moderate light intensity, while the latter one allows spectrum retrievals without switching on/off the probe comb intensity, but rather by excitation of the cavity with comb-cavity amplitude or phase noise. In a demonstration probing methane as an analyte, we show consistency between the retrieved absorption and dispersion spectra. Our DC-CRDS technique combines all the advantages of conventional CRDS with a parallel broadband measurement. Also, the simplicity of the DC-CRDS cavity excitation and detection schemes should make the method attractive for many applications in molecular spectroscopy.

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Cavity mode-dispersion spectroscopy applied in saturation conditions

K. Bielska[1], A. Cygan[1], M. Konefał[1], G. Kowzan[1], M. Zaborowski[1], D. Charczun[1], S. Wójtewicz[1], P. Wcisło[1], P. Masłowski[1], R. Ciuryło[1]*, D. Lisak[1]*

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland

Highly accurate molecular spectroscopy, apart from multiple applications in remote sensing, provides tools for tests of fundamental physics, such as quantum electrodynamics (QED) tests [1] and determination of physical constants variability [2]. Transition frequencies can also be used as frequency standards for metrological applications if they are determined with sufficient accuracy [3].

Cavity mode-dispersion spectroscopy (CMDS) [4] of Doppler-broadened transitions has high accuracy in a wide dynamic range compared to cavity ring-down spectroscopy (CRDS) and cavity mode-width spectroscopy (CMWS) [5]. In the present work, we demonstrate its application to Lamb-dip spectroscopy. The comparison with CRDS and CMWS again shows a predominance of the dispersive technique, which leads to the most accurate determination of the Lamb dip frequency. Neither CRDS nor CMWS is capable to show an evident absorption dip in the entire range of conditions covered by CMDS.

Here the CMDS technique is used to measure unperturbed frequencies and pressure shift of transitions from the 2nd overtone of CO near 1.57 µm. We determine line positions with sub-kHz accuracy. In contrast to the literature data [6], we detect non-zero pressure shift of transitions under investigation in saturation conditions.

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Molecules probed with a slow chirped-pulse excitation: analytical model of the free-induction-decay signal

G. Dhont[1], D. Fontanari[1], C. Bray[1], G. Mouret[1], A. Cuisset[1], F. Hindle[1], R. Bocquet[1], K. Hickson[2]

[1]Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France, [2]Institut des Sciences Moléculaires, Université de Bordeaux, Talence, France

A chirped pulse experiment is a powerful means to rapidly obtain an high-resolution spectrum of molecules on a large frequency band. The theoretical paper from McGurk *et al.* [1] is the main reference paper to describe the polarization induced by fast chirped pulses generated with microwave sources.

We built a chirped pulse spectrometer operating at 200 GHz for atmospheric and astrophysical applications [2]. It works in the millimeter domain with slower chirped pulses. In such a situation, the paper of McGurk *et al.* does not capture all the physics involved in the polarization step. In particular, the intensity of a molecular transition is dependent on its temporal position inside the chirped pulse, as discovered by Abeysekera *et al.* [3].

A theoretical study of the polarization of molecules subjected to a slow chirped pulse is presented for three typical cases: the cell, the uniform flow and the molecular beam. Analytical expressions are proposed alongside the numerical solution and are used in the expression of the free induction decay signal. We test the analytical expression on the rotational emission spectra of OCS molecules. In the thermalized case, a relation between the pulse duration, the line position in the chirped pulse, and the signal amplitude is proposed to correct the line intensities [4].

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Potential energies and electronic dipole transition moments of confined hydrogen in spheroidal boxes

S. Bezzaouia[1], H. Abbassi[1], M. Telmini[1]*

[1]Laboratory of Atomic Molecular Spectroscopy and Applications

The study of spatial confinement of quantum systems is of great interest these decades especially with the advent of modern techniques for the synthesis of nanostructured materials in order to allow molecular insertion and storage. The behavior of electronic and structural properties of a confined atom or molecule is studied in comparison to their free counterparts. The typical confining potentials are spherically symmetric, cylindrical or spheroidal. Confined hydrogen in its neutral, ionic and molecular forms has been the subject of several studies using different theoretical methods [1]. These studies are limited to low excited states for the atomic hydrogen and molecular ion and to the ground state in equilibrium bond length for molecular hydrogen beyond the Born-Oppenheimer approximation. We are interested in the effect of spatial confinement in a hard prolate spheroidal box on potential energies and electric dipole transition moments of hydrogenic systems and . To realize this study, we used an *ab initio* variational R matrix method which enables ground and excited states of diatomic systems to be calculated for fixed nuclei on the foci of the spheroidal box [2]. In this contribution, potential energies and electric dipole moments are evaluated within the Born-Oppenheimer approximation for internuclear distances and for different spheroidal box sizes. To validate our theoretical approach, potential energies and electronic dipole transition moments are calculated first in a very large cavity to simulate the situation of the free case for and . The results are then compared to the best available ones [3]. An overall agreement is obtained.

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Finding an Alien Biosphere with Computational Chemistry

C. Sousa-Silva[1]

[1]Harvard-Smithsonian Center for Astrophysics, Cambridge, US - csousasilva@cfa.harvard.edu

At the edge of our present scientific frontier lies the question: “Can we identify the signs of life on an exoplanet?”. Establishing whether a planet is habitable, or inhabited, relies both on the observation of an exoplanet atmosphere and, crucially, its subsequent interpretation. This interpretation requires knowledge of the spectral behavior of every significant atmospheric molecule. However, though thousands of molecular candidates can contribute towards the spectrum of an atmosphere, data exist for only a few hundred gases. Among these, only a fraction have complete spectra (e.g. ammonia, water). This deep incompleteness in the knowledge of molecular spectra presents a pressing vulnerability in the atmospheric study of planets; there exists a strong possibility of mis-assignment, false positives, and false negatives in the detection of molecules.

The work presented in this talk combines structural organic chemistry and computational quantum mechanics to obtain the necessary tools for the interpretation of astrophysical spectra and, ultimately, the detection of life on an exoplanet. Whether alien life will produce familiar gases (e.g., oxygen) or exotic biosignatures (e.g., phosphine), painting a confident picture of a potential biosphere will require a holistic interpretation of an atmosphere and its molecules. In this talk Clara will describe ongoing efforts to train the next generation of scientists to decipher exoplanet atmospheres, and ultimately to detect a biosphere through the identification of volatile molecules, in particular those that might be produced by non-Earth-like life.

High-precision molecular spectroscopy referenced to frequency standards at the 10^{-14} level

A. Amy-Klein[1]

[1]Laboratoire de Physique des Lasers, Université Sorbonne Paris Nord, CNRS, Villetaneuse, France

Coauthors : D.B.A. Tran[1], R. Santagata[1,2], E. Cantin[1], O. Lopez[1], M. Tønnes, N. Cahuzac[1], M. Manceau[1], M. Abgrall[2], Y. Le Coq[2], R. Le Targat[2], H. Alvarez-Martinez[2], D. Xu[2], P.-E. Pottie[2], B. Darquié[1]

1. Laboratoire de Physique des Lasers, Université Sorbonne Paris Nord, CNRS, Villetaneuse, France; 2. LNE-SYRTE, Observatoire de Paris, Université PSL, CNRS, Sorbonne Université, Paris, France.

High-precision measurements with molecules may refine our knowledge of various fields of physics, from atmospheric and interstellar physics to the standard model or physics beyond it. Many of them can be cast as absorption frequency measurements, particularly in the mid-infrared molecular fingerprint region, creating the need for narrow-linewidth lasers of well-controlled frequency.

In order to reach the higher precision, we need to go beyond a reference to GNSS. In my talk I will show recent developments on frequency dissemination by optical fiber links. They provide the opportunity to transfer an ultrastable frequency reference elaborated in a National Metrological Institute (NMI), where it is controlled to frequency standards, to any physics lab provided they are connected with an optical fiber. This signal can then be used to control the repetition rate of an optical frequency comb, and the spectroscopic laser is then phase-locked to one mode of this comb. This opens the way to SI-traceable high-resolution molecular spectroscopy, as already demonstrated using national metrological networks in France and Italy.

In France, we are building a national metrological network, called REFIMEVE, to disseminate an ultrastable laser at 1,5 µm generated at LNE-SYRTE to more than twenty laboratories over France [1]. It was used at LPL to perform precise spectroscopy in the mid-infrared with Quantum Cascade Lasers (QCL) emitting at 10 µm [2,3]. After frequency stabilisation using the REFIMEVE signal, the QCL exhibits a relative frequency stability lower than 2×10^{-15} between 1 and 100 s and its absolute frequency is known with an uncertainty below 10^{-14} thanks to the traceability to the primary standards of SYRTE [4]. The setup allows the QCL to be widely tuneable while maintaining the highest stabilities and accuracies. This is achieved by scanning the near-infrared reference laser over ∼10 GHz using an electro-optic modulator which in turn allows the QCL to be tuned over ∼1.4 GHz.

With this stabilised QCL we performed saturated absorption spectroscopy of some C-O stretching vibrational transitions of methanol contained in a multipass cell at low pressure around 1 Pa [3]. We reached a statistical uncertainty at the kHz level on the transition centre frequencies and determined the frequencies with uncertainties as low as 7 kHz limited by systematic effects. Some of the lines we measured were not reported so far and we were also able to resolve for the first time some K-doublets. We also performed precision spectroscopy of trioxane and ammonia. This stabilisation set-up to a remote frequency standard is also a key technology for our on-going measurement of the tiny energy difference between enantiomers of a chiral molecule induced by electroweak interactions, a signature of parity (left-right symmetry) violation [5].

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Program, Friday, September 3, 2021

12.00	**Poster Session 2** Watch the short video presentations Meet the poster presenters on the interactive platform MeetAnyway
13.30	Break
	Invited Lectures (O) Chair: Frédéric Merkt, ETH Zürich, Switzerland
14.00	**Amat-Mills Prizes**
14.10	***Henrik G. Kjaergaard***, University of Copenhagen «Accurate Gibbs Energies of Complex Formation»
14.55	***Thomas R. Rizzo***, Ecole Polytechnique Fédérale de Lausanne «Cryogenic Vibrational Spectroscopy of Conformationally Selected Biomolecules»
15.30	Break
	Mini-Symposium 3: Environmental and Atmospheric Spectroscopy (P) Chair: Thérèse Huet, Université de Lille, France
16.00	***Georg Wagner***, German Aerospace Center, DLR «FT spectroscopy in support of atmospheric spectroscopic databases: Recent advances at DLR»
16.30	***Agnes Perrin***, UMR CNRS 8539 «Molecules of Tropospheric or Stratospheric Interest: From Laboratory Spectroscopy to Satellite Applications»
17.00	***Didier Mondelain***, Université Grenoble Alpes, CNRS «Molecular spectroscopy by laser techniques for the study of planetary atmospheres»
17.30	***Lilian Joly***, Université de Reims Champagne-Ardenne «AMULSE " Atmospheric Measurements by Ultra Light SpEtrometer " - Greenhouse gas measurements under tethered balloons, weather balloons and drones»
18.00	End of HRMS 2021

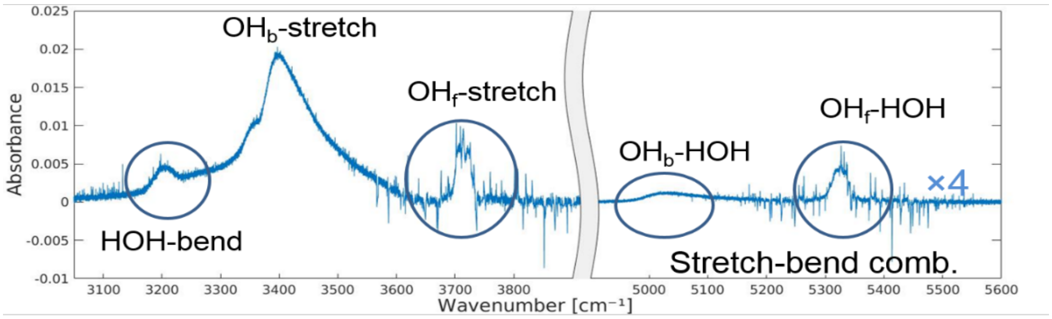
Accurate Gibbs Energies of Complex Formation

H. G. Kjaergaard[1], E. Vogt[1], A. Kjærsgaard[1]

[1]Department of Chemistry, University of Copenhagen, Denmark

The formation of a molecular complex relies on the Gibbs energy of formation, ΔG, which is often difficult to obtain accurately from pure experimental or theoretical methods. A hydrogen bound bimolecular complex consists of a hydrogen bond donor and acceptor unit. The OH-stretching fundamental transition of the hydrogen bond donor is typically redshifted and its infrared intensity enhanced upon complexation.[1] This facilitates detection of weak complexes even though the equilibrium is strongly shifted towards the monomers at room temperature. The ratio of a measured and calculated intensity of a vibrational band is proportional to the complex abundance, which with known monomer pressures gives the equilibrium constant.[2,3] We have developed a reduced dimensionality variational local mode model, which includes both high- and low-frequency vibrations, and we use this model to calculated absolute transition intensities.

We have used this combined experimental and theoretical approach for a number of bimolecular complexes and recently extended it to hydrated complexes. The spectrum of the water-trimethylamine complex is shown in the figure.[3] The equilibrium constant obtained from the observed five different bands should be equivalent, and the detection of multiple bands therefore allows us to validate the accuracy of our combined experimental and theoretical approach. We believe the accuracy of ΔG for the water-amine complexes is better than 1 kJ/mol.[3]



The water dimer, H_2O-H_2O, is an atmospherically important hydrogen bound complex. Most spectroscopic studies on water dimer are performed under non-equilibrium cold conditions, which favor complex formation; however, in an atmospheric context information at ambient temperature is important. As a first step, we have recently developed a variational local mode model for water dimer that include all six intramolecular modes and the three most important intermolecular modes. The calculated fundamental vibrational transition frequencies and relative intensities agree well with results from jet-cooled experiments.

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Cryogenic Vibrational Spectroscopy of Conformationally Selected Biomolecules

T. R. Rizzo[1], S. Warnke[1], A. Ben Faleh[1], I. Dyukova[1], P. Bansal[1]

[1]Ecole Polytechnique Fédérale de Lausanne, Laboratoire de chimie physique moléculaire, Station 6, CH-1015 Lausanne, Switzerland

Vibrational spectroscopy of biological molecules is complicated by the coexistence of multiple stable conformers and/or isomers, which causes spectral congestion and hinders analysis, even at low temperatures. Spectroscopic schemes such as IR-UV double resonance or IR-IR hole burning can help deal with this conformational or isomeric heterogeneity in favorable cases, but neither is universally applicable. New spectral simplification methods are thus needed to push vibrational spectroscopy to increasingly complex biological molecules in a meaningful way. One class of molecules for which this is particularly important is that of glycans, or sugars.

Despite their biological importance, glycans present a particular problem for analysis arising from the multiple types of isomerism that are simultaneously present. Orthogonal techniques need to be applied simultaneously to have any chance of resolving their isomeric complexity. The most common approach is to combine liquid chromatography (LC) with mass spectrometry (MS), but LCMS cannot distinguish the subtlest isomeric forms. Ion mobility spectrometry (IMS) is being increasingly applied to glycan analysis, but even this powerful technique cannot completely distinguish subtly different isomers. Vibrational spectroscopy, on the other hand, is exquisitely sensitive to the smallest difference between isomeric species, particularly when performed at cryogenic temperatures.

We have recently developed a technique that combines ultrahigh-resolution ion mobility spectrometry with cryogenic ion vibrational spectroscopy for the analysis of gas-phase biological ions, and we have been applying it principally to glycans (1-3). We achieve extremely high-resolution ion mobility using structures for lossless ion manipulations (SLIM) (4), which employs traveling-waves generated between a closely spaced pair of printed circuit-board electrodes. Because ions can be made to follow a serpentine path, one can achieve ultra-long separation lengths, and hence extremely high resolution, in a compact instrument. This allows us to separate glycan isomers that differ only by the orientation about a single stereogenic center. After mobility separation, we then record a vibrational fingerprint at cryogenic temperatures using messenger-tagging spectroscopy and compare it with a database constructed from suitable standards.

We will demonstrate here the power of this technique by applying it to a series of glycans of increasing complexity and show the steps we are taking towards making this approach into a high-throughput analytical tool.

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FT spectroscopy in support of atmospheric spectroscopic databases: Recent advances at DLR

G. Wagner[1], M. Birk[1], J. Loos[1], C. Röske[1]

[1]German Aerospace Center, DLR, Münchner Str. 20, D-82234 Wessling

High resolution Fourier-Transform spectroscopy of atmospheric trace gas has been carried out at DLR since 1990. The primary focus is on supplying well characterized uncertainties. The core instrument is the commercial high-resolution Bruker IFS 125 HR Fourier-transform spectrometer operating from 10 to 40000 cm^{-1}. The laboratory infrastructure has been continuously improved over the last 30 years, especially the absorption cells. A 22 cm absorption path 200-350 K cell features two windows pairs allowing quasi-simultaneous measurement from FIR to UV. A 200 m absorption path multireflection cell operates in the temperature range 200-350 K with high temperature homogeneity. Line fitting software was steadily improved, resulting in a multispectrum fitting tool with several line shape models including the Hartmann-Tran profile. The instrumental line shape of the Fourier-transform spectrometer is adopted from the LINEFIT software by Frank Hase, IMK, which is also used by the TCCON community.

Recent results are a spectroscopic database of the O_3 fundamentals and temperature dependent UV absorption cross sections for O_3, together solving the 4% discrepancy between UV and MIR atmospheric O_3 columns, a comprehensive H_2O spectroscopic database in the range 1850-4300 cm^{-1}, a new method to obtain H_2O continua, H_2O foreign- and self-continua in the 3 µm region, and a CO_2 database in the range 6000-7000 cm^{-1} with absolute intensity uncertainties <0.15%. Most of these results have become part of the HITRAN20 database.

Molecules of Tropospheric or Stratospheric Interest: From Laboratory Spectroscopy to Satellite Applications

A. Perrin[1,5], L. Manceron[2,6], R. Armante[1,5], F. Kwabia-Tchana[3,7], P. Roy[2], D. Doizi[4,8]

[1]Laboratoire de Météorologie Dynamique/IPSL, [2]Synchrotron SOLEIL, AILES Beamline, [3]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), [4]Den-Service d'Etude du Comportement des Radionucléides (SECR), [5] Ecole Polytechnique, Palaiseau, France, [6]MONARIS, [7]Université de Paris et Université Paris Est Créteil, IPSL, [8]Université Paris-Saclay

Remote sensing in the infrared region is a very powerful technique for observing atmospheric composition, either from satellite, balloon borne or ground-based systems. However, together with an accurate radiative transfer code, the analysis and interpretation of the atmospheric spectra require good knowledge of the molecular parameters of the species of interest as well as of the interfering species. This is particularly true for the recent instruments which cover wide spectral ranges at rather high spectral resolutions with excellent signal to noise ratios. The present talk will describe spectroscopic analyses which lead to improved line positions and intensities for several molecules of stratospheric or tropospheric interest. Through these examples it will be demonstrated that improving the quality of the spectroscopic parameters leads to a better interpretation of the atmospheric spectra.

Molecular spectroscopy by laser techniques for the study of planetary atmospheres

D. Mondelain[1], A. Campargue[1], H. Fleurbaey[1], S. Kassi[1], S. Vasilchenko[2]

[1]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France , [2]AV.E. Zuev Institute of Atmospheric Optics, SB, Russia

It is becoming essential to probe certain molecular species of the Earth's atmosphere with very high precision. This is particularly true for greenhouse gases (CO_2, CH_4) in the context of satellite missions such as *OCO-2*, *MicroCarb*, *MERLIN* and will become so for other molecules thanks to the launch of new generations of satellites, requiring higher and higher quality spectroscopic data. Dedicated laboratory measurements are performed in support of these missions in order to provide spectroscopic parameters of the targeted absorption lines and their temperature dependence with reduced uncertainty. It is therefore necessary to record spectra with high signal-to-noise ratios (> 1,000) and to fit these spectra with non-Voigt line profiles including effects such as velocity dependence and collisional narrowing. In this talk, I will present our previous and ongoing works by Cavity Ring Down Spectroscopy of O_2 (~1.27 µm), CO_2 (~1.60 µm) and CH_4 and water vapor (~1.65 µm) in support of the *MicroCarb* and *MERLIN* missions (CNES and DLR) and the *ISOGG* program of ESA.

The second part of my talk will be devoted to the measurements of absorption continua of H_2O and H_2 mixed with CO_2. Indeed, measuring and modeling accurately the infrared absorption spectra of these mixtures and their temperature dependences is of great importance for planetary sciences (in particular Mars). The spectra recorded by CRDS and OFCEAS include a contribution due to the local absorption by the rovibrational lines of each species, which can be calculated from spectroscopic databases, and a broadband contribution (namely the continua). The continua are poorly characterized but crucial to account for the radiative budget and the composition of planetary atmospheres, and hence to accurately model the formation, evolution, and present atmospheric state of telluric planets from the solar system and beyond.

AMULSE " Atmospheric Measurements by Ultra Light SpEtrometer " - Greenhouse gas measurements under tethered balloons, weather balloons and drones

L. Joly[1]

[1]GSMA, UMR CNRS 7331, Université de Reims, U.F.R. Sciences Exactes et Naturelles, 51687 Reims Cedex 2 - lilian.joly@univ-reims.fr

We are all aware of the increase in greenhouse gas (GHG) emissions and their impact on the climate. The median assumptions of the Intergovernmental Panel on Climate Change (IPCC) predict a doubling of carbon dioxide (CO_2) before the end of this century. But the concentration of other greenhouse gases with a radiative power greater than that of CO_2increases, such as for example methane (CH_4). According to the IPCC, reduction in greenhouse gas emissions must accelerate by 2030 to have any chance of achieving the goal of keeping the increase in global temperature below +1.5°C. To limit our impact, it is therefore crucial to properly quantify the sinks/sources of the different types of industrial and natural ecosystems. The monitoring and quantification of atmospheric emissions are key points in this reduction challenge.This is why the GSMA (Groupe de Spectrométrie Moléculaire et Atmosphérique - France) is working on the development of a laser diode spectrometer called AMULSE (Atmospheric Measurements by Ultra Light SpEtrometer) to help better quantify greenhouse gas emissions. Different versions of AMULSE exist to make measurements from the ground, weather balloon and drone. This presentation will present the instrument, the applications and the results but also the different perspectives in the framework of the joint laboratory and the industrial chair with TotalEnergies.