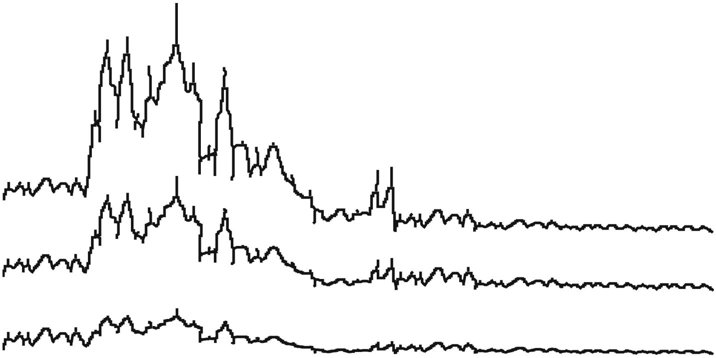
Book of abstracts

of the 26$^{\text{th}}$ International Conference
on High Resolution Molecular Spectroscopy



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on High Resolution Molecular Spectroscopy

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J6 **Sanz M. E.** 10:00
Burevschi E., Chrayteh M., Loru D., Murugachandran S. I., Dréan P.
Multiple Water Configurations in Fenchone-$(H_2O)_{1\text{-}7}$ Hydrates Revealed by Rotational Spectroscopy

Session K - Contributed Lectures Friday, 10:40

chairperson: Maria Eugenia Sanz

K1 **Balashov A. A.** 10:40
Tretyakov M. Yu., Serov E. A., Makarov D. S., Vilkov I. N., Golubyatnikov G. Yu., Galanina T. A., Koshelev M. A., Simonova A. A., Thibault F.
R(0) and R(1) Rotational Lines of the CO Molecule in Ar Bath: Experimentally Measured Collisional Parameters versus Ab initio Calculations

K2 **Claus J. A.** 10:58
Bermúdez C., Goubet M., Margulès L.
The Hydration of Polycyclic Aromatic Compounds: the Case of Naphthaldehyde

K3 **Hazrah A. S.** 11:16
Insausti A., Ma J., Al-Jabiri M., Xu Y., Jäger W.
Microsolvation vs Droplet Aggregation: A Broadband Rotational Spectroscopic Study of 3-methylcatechol Water Complexes

K4 **Melandri S.** 11:34
Maris A., Evangelisti L., Lv D. , Song W., Maggio A., Elliott A. A., Peebles S. A., Peebles R. A., Neill J. L., Muckle M. T., Pate B. H.
σ-hole Activation and Structural Changes upon Perfluorination of Aryl Halides: Direct Evidence from Gas Phase Rotational Spectroscopy

K5 **Osseiran N.** 11:52
Neeman E. M., Dran P., Goubet M., Damart H., Dekyndt G., Huet T. R.
Microwave Study of α-pinene-oxide with the New CP-FTMW Spectrometer in Lille

K6 **Crehuet O.** 12:10
Insausti A., Parra M., Alonso E. R., Cocinero E. J.
Conformational Study of the Synthetic Repellents DEET and Picaridin to Improve Structure-based Design of Novel Mosquito Repellents

K7 **Dohmen R.** 12:28
Pincho P., Kempken B., Schnell M., Obenchain D.
Microwave Study of H_2 in Complexes with Small Aromatic Molecules

Session A

Invited Lectures

August 30, Tuesday, 8:30 – 10:00

Towards Artificial Olfaction:

From High Resolution Spectroscopy to Multi-Scale Computational Methods

Halima Mouhib

Vrije Universiteit Amsterdam, VU Bioinformatics, Computer Science Department, The Netherlands, h.mouhib@vu.nl

The study of the olfactory sense is a multi-disciplinary challenge that requires research at the interface of biology, chemistry, and physics. Entangling the complexity of the molecular mechanisms underlying the sense of smell opens up a wide field of applications ranging from structure-odor predictions of molecules[1] to the development of artificial sensors[2] for the detection of biomarkers in medical prevention and industrial production chains. Despite numerous efforts to design novel gas sensors for odorants and other volatile organic compounds, the current state-of-the-art is still far from providing efficient devices that can act as electronic artificial noses. One problem currently holding back the advancement in the field is our fragmentary understanding of the key detection mechanisms in olfaction.

To characterize odorant uptake from the gas-phase to the solvated protein environment, which is the first step involved in the process, a multi-scale approach using adapted computational methods combined with reliable experimental techniques is required. One of the objectives is to unravel how odorants vary in their conformational flexibility in the gas phase and in the solvated phase, to quantify their uptake mechanisms by odorant binding proteins. Hereby, valuable insight can be obtained from high-resolution microwave spectroscopy experiments in combination with quantum chemical calculations to characterize the most abundant conformations of odorants in the gas-phase.[3] To quantify the (un)binding mechanisms of the protein complex in the solvated phase, molecular dynamics and enhanced sampling techniques are required,[4,5] with the aim to predict new protein candidates of increased molecular selectivity and sensitivity to detect odorants in artificial noses. In future, due to the increasing number of available data on molecular structures and olfactory properties, more data-driven approaches will be necessary to address new computational challenges and thus, in the long term, allow us to move towards the digitization of the olfactory sense.[6,7]

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Ultrahigh resolution spectroscopy and ultrafast molecular dynamics using ultrashort intense laser pulses

Kaoru Yamanouchi

Department of Chemistry, School of Science, The University of Tokyo, Japan

When hydrocarbon molecules are exposed to an intense laser field, they exhibit a variety of characteristic dynamical processes such as ultrafast hydrogen atom migration and ejection of a triatomic hydrogen molecular ion, H_3^+ [1-4]. We revealed that the yield of H_3^+ exhibits a long-lasting periodic increase reflecting the motion of the vibrational wave packet in methanol cation along the C-O bond stretching coordinate, showing that the time-resolved measurement of the yields of fragment ions is an efficient tool not only for probing ultrafast nuclear dynamics of molecular cations but also for deriving their vibrational frequencies [5]. We performed pump-probe measurements of methanol and its isotopologues, and obtained the vibrational mode frequencies of methanol and methanol cations by Fourier transform (FT) of the yields of the parent ion and the fragment ions recorded as a function of the pump-probe delay time [6].

By taking advantage of the fact that the resolution of a FT spectrum can be raised by extending the pump-probe delay time, we performed pump-probe measurements of the yields of D_2^+ and D^+ produced after the photoionization of D_2 using ultrashort intense near-IR few-cycle laser pulses up to the pump-probe delay time of 527 ps and determined the vibrational level separations of D_2^+ with uncertainties as high as 0.0002 cm^{-1}, showing a potential applicability of strong-field ultrahigh resolution FT (SURF) spectroscopy of molecular ions [7]. We also applied SURF spectroscopy to the determination of the spin-orbit splitting of Ar^+ and Kr^+. By the FT of the yields of Ar_2^+ and Kr_2^+ obtained by the pump-probe measurements using intense near-infrared few-cycle laser pulses, we determined the spin-orbit splitting energies in the electronic ground states of Ar^+, Kr^+, and Kr^{2+} with high precision. The $^2P_{1/2} - {}^2P_{3/2}$ spin-orbit splitting energies of Ar^+ and $^{84}Kr^+$ were determined to be 1431.583 33(12) and 5370.296 42(50) cm^{-1}, respectively, and the isotope effect was examined for $^{83}Kr^+$, $^{84}Kr^+$, and $^{86}Kr^+$ [8]. We further extended the pump-probe time delay up to 6 ns and determined the fundamental vibration frequency of H_2 with an uncertainty 3 times as small as that achieved before by high-resolution spectroscopy.

We also recorded the time-dependent yields of the two-body Coulomb explosion pathway, $H_2O^{2+} \rightarrow H^+ + OH^+$, and the parent ion, H_2O^+ and obtained the SURF spectra. Based on the phases of the respective vibrational peaks in the SURF spectra, we examined the vibrational wave packet dynamics in the electronic ground states of H_2O^+ and H_2O induced by the intense laser field [9].

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Session B

Memorial session

August 30, Tuesday, 10:30 – 12:00

In Memory of Jon, Jim, Manfred, Andrei, and Per
The Loss of Legends

Vladimír Špirko

Institute of Organic chemistry and Biochemistry, Czech Academy of Sciences,
Flemingovo nám. 542/2 , 160 00 Prague 6, Czech Republic

A tribute is paid to the legends of this conference that we have lost in the time that has passed since its last event.

Group theoretical treatment of n-methylated (n = 2 - 4) aromatic rings using the semi-direct product

Ha Vinh Lam Nguyen[1,2]

[1]*Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France*
[2]*Institut Universitaire de France (IUF), F-75231 Paris, France*
lam.nguyen@lisa.ipsl.fr

In memory of Jon T. Hougen and Per Jensen.

If a molecule with C_{2v} point-group symmetry at equilibrium undergoes internal rotations of two equivalent methyl groups (n = 2), its molecular symmetry group is G_{36}. There are different symmetry labels in use which arise from different product decompositions of G_{36}. Probably, the earliest method is based on the direct product $\boldsymbol{C_{3v}^-} \times \boldsymbol{C_{3v}^+}$, and the symmetry species of G_{36} are labeled with the labels of both subgroups $\boldsymbol{C_{3v}^-}$ and $\boldsymbol{C_{3v}^+}$ [1]. Using the permutation-inversion group formalism, Bunker and Jensen derived a character table of acetone, where the different species are denoted by their degeneracy letter A, E, G and a running index with the well-known irreducible representations A1, A2, A3, A4, E1, E2, E3, E4, and G [2]. A third labelling scheme is introduced where G_{36} is written as the semi-direct product $(\boldsymbol{C_3^I} \times \boldsymbol{C_3^I}) \rtimes \boldsymbol{C_{2v}}$, as reported by Ezra [3]. The theoretical background was described in detail also by Altmann [4].

The direct product $\boldsymbol{C_3^I} \times \boldsymbol{C_3^I}$ of the two intrinsic (superscript I) $\boldsymbol{C_3}$ groups of the internal rotors, which is an invariant subgroup of G_{36}, decomposes into four orbits under $\boldsymbol{C_{2v}}$. One representative of each orbit forms the first part of the symmetry label, e.g. (01). The numbers $\sigma = 0, 1, 2$ represent the three symmetry species A, E_a, E_b, respectively, of the group C_3 and correspond to the transformation properties of the C_3-adapted planar rotor wave functions $\boldsymbol{e^{i(3k+\sigma)\varphi}}$ with $\boldsymbol{k} \in \mathbb{Z}$ and the torsional angle $\boldsymbol{\varphi}$. Each orbit is associated with its little co-set. They form subgroups of C_{2v}. The symmetry species of the little co-sets provide the second part of the symmetry labels. These symmetry labels were used to treat 2,5-dimethylthiophene [5], 2,6-dimethylfluorobenzene [6], and 2,5-dimethylpyrrole [7] group theoretically. The semi-direct product concept is also applied to treat 2,6-dimethylanisole (n = 3, C_s, G_{54}) and tetramethylthiophene (n = 4, C_{2v}, G_{324}) [8].

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Leak-Out Spectroscopy, a New Method of Action Spectroscopy in Cold Ion Traps

Philipp Schmid[1], Oskar Asvany[1], Sven Thorwirth[1], Thomas Salomon[1] and Stephan Schlemmer[1]

[1]*I. Physikalisches Institut, Universität zu Köln, Germany, schlemmer@ph1.uni-koeln.de*

Action spectroscopy in ion traps developed into a mature method to study the spectra of molecular ions.[1] In most cases the action lies in changing the mass of the ion either by fragmentation upon multiple photon absorption, pre-dissociation of a tagged molecule or chemical reactions which all lead to a change in the composition of the stored ion cloud. Major benefits of this approach lie in the mass selective preparation of cold ions of interest, the mass analysis of the product ions and the near unit detection efficiency of ions. Despite these advancements the spectra of many ions cannot be recorded when the above methods cannot be applied. For this, e.g., the light intensity might be too weak for the absorption of multiple photons or the tag atom leads to unwanted spectral shifts or a suitable neutral reaction partner is not known to promote a chemical reaction.

Here, we introduce a new method of action spectroscopy overcoming these limitations. In one realization of this experiment we store mass selected linear l-C_3H^+ in a cryogenic 22-pole ion trap and excite those ions with light from a cw infrared OPO (Toptica TOPO) to excite the ν_1 C-H stretching vibration. This process adds more than 3000 cm^{-1} of internal energy to the molecule. In a subsequent collision with N_2 a considerable fraction of the internal energy is converted to translational energy of both collision partners. By adjusting the electrical potential of the exit electrode of the trap these fast ions leave the trap which we record as a leak-out signal of the parent l-C_3H^+. This is why we term this method leak-out spectroscopy (LOS).[2] In the present case we obtain a ro-vibrationally resolved spectrum of cold l-C_3H^+. The method can be applied to virtually any ion of interest. We applied this idea to several molecular ions and to various vibrational modes. We also showed that a pulsed nanosecond OPO light source leads to a LOS signal. Using millimeter-IR double-resonance also pure rotational transitions have been measured. The LOS technique relies on the vibration-to-translation energy transfer which adds enough energy to the ion to leave the trap but also electronic transitions might be used.

In each experimental cycle a finite number of mass selected ions is stored. If this ensemble consists of different isomers, conformers or nuclear spin isomers, only the one species addressed by the interacting light will lead to a leak-out signal and the other species remain in the trap. As a result, the isomer composition of the ion cloud can be analysed and/or leak-out of unwanted species can be used to prepare an isomer clean sample. As a first example, we prepared pure samples of ortho-H_3^+ (o) and para-H_3^+ (p) by kicking the other species out of the trap exciting a ro-vibrational transition. By these means we determine the o/p ratio of H_3^+. Moreover, employing leak-out state-specific processes can be studied, e.g., the ortho to para transitions o-H_3^+ + p-H_2 => products and p-H_3^+ + p-H_2 => products are getting in reach. Likewise, isomer specific reactions can be studied. Thus, leak-out spectroscopy in cryogenic ion traps is opening a new door to cold ion chemistry.

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How to compute accurate rovibronic spectra of open-shell diatomic molecules

Sergei N. Yurchenko

Department of Physics and Astronomy, University College London, London, United Kingdom, s.yurchenko@ucl.ac.uk

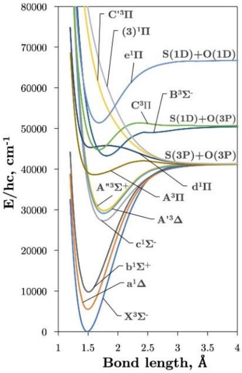

Figure 1 Diabatic ab initio potential energy curves of SO

An efficient methodology for computing accurate rotational, rovibrational and rovibronic spectra of diatomic molecules based on high level ab initio and nuclear motion calculations will be presented.

Consider a general diatomic system consisting of (strongly interacting) electronic states covering a large spectroscopic range as illustrated in Fig. 1. It is typical for such systems to have a complex network of interactions involving spin-orbit and electronic angular momentum couplings, exhibiting non-adiabatic and tunneling effects and highly excited electronic bands dominated by photo-dissociation. Modern high-resolution applications require that all these effects are accurately treated when computing rovibronic spectra.

We have developed a rovibrational diatomic code Duo written in the modern Fortran to solve a fully coupled set of rovibronic Schrodinger equations for an arbitrary diatomic system [1]. Duo is a part of the ExoMol toolbox, developed for production of accurate and complete molecular line lists for atmospheric and astrophysical applications [2] and freely available on GitHub [3]. Duo is equipped with a fitting module to empirically refine potential energy curves (PECs), spin-orbit curves (SOCs) and other couplings. Duo is capable of computing bound-bound and bound-continuum [4] spectra with or without hyperfine [5] effects, based on *ab initio* dipole and quadruple moment curves (DMCs and QMCs) and accurate Duo rovibronic wavefunctions.
Different technical aspects of our diatomic computation protocol will be discussed, including non-adiabatic effects, importance of relative phases of electronic wavefunctions, treatment of continuum vibronic wavefunctions in UV spectra, interactions with dark states, empirical refinements and MARVELisaions. Illustrations of recent applications will be given.

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Session C

Contributed Lectures

August 30, Tuesday, 14:15 – 16:20

Ion-neutral and dissociative recombination reactions of CO, H_2CO, HCO^+ and H_3^+: Observational and theoretical implications in Star Forming Regions

<u>Edgar Mendoza</u>[1], Leonardo Bronfman[2], Miguel Carvajal[1], Manuel Merello[2], Heloisa M. Boechat-Roberty[3]

[1]*Departamento de Ciencias Integradas, Universidad de Huelva, Spain, edgar.mendoza@dci.uhu.es;*[2]*Departamento de Astronomía, Universidad de Chile, Chile;*
[3]*Observatório do Valongo, Universidade Federal do Rio de Janeiro, Brazil*

In the Insterstellar Medium, species as formaldehyde (H_2CO) and the formyl cation (HCO^+) are demonstrated to be useful to analyse various physical and chemical properties in high-mass star-forming regions, among them: *i.* mechanisms of excitation, *ii.* isotopic enrichment, and *iii.* gas-grain chemical processes. Thus, here we present results on the detection of H_2CO and HCO^+, along with their D, ^{13}C and ^{18}O isotopologues, in the context of hot molecular core and outflow systems [1].

The astronomical observations are based in a dataset collected, in the frequency range ~160-350 GHz, with the Atacama Pathfinder Experiment telescope [2]. The chemical formation, destruction and stability of H_2CO and HCO^+ were computed using kinetic and quantum chemical calculations.

Transitions of H_2CO, $H_2{}^{13}CO$, HDCO and $H_2C^{18}O$ were identified (e.g. Fig. 1a), their spectral emissions suggest a bulk gas with temperature $T \sim 20$-100 K. Spectra of HCO^+, $H^{13}CO^+$, $HC^{18}O^+$ and $HC^{17}O^+$were also observed (e.g. Fig. 1b), however their analyses suggest a colder gas component with $T < 20$ K. Such scenario is evaluated in a gas-grain chemical model [3] using a grid of gas density and temperature values (e.g. Fig. 1c). We also present results about the $^{12}C/^{13}C$, H/D and $^{16}O/^{18}O$ ratios. In particular, it was possible to estimate molecular deuteration through the H_2CO/HDCO ratio but not from the HCO^+/DCO^+ one. Considering that the DCO^+ presence relies on the availability of, e.g., D_3^+, H_2D^+ and free electrons [4], we discuss its abundance in terms of those molecular ions, H_2 densities and the evolutionary stage of massive protostellar objects.

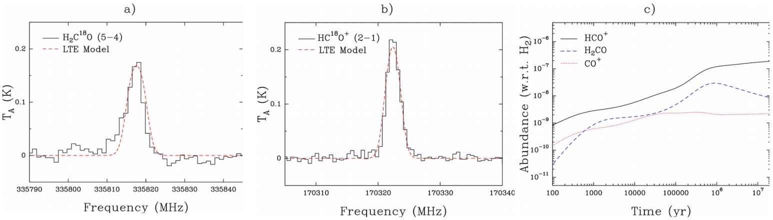

Fig. 1: Spectral lines and models of a) $H_2C^{18}O$ and b) $HC^{18}O^+$; c) Predicted abundances of HCO^+, H_2CO and CO^+.

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Re-visiting the A-X system of CrH to help analyse polarimetric spectra of cool, magnetically active dwarf stars

Amanda Ross[1], Léa Collignon[1], Arthur Talarmin[1], Patrick Crozet[1] and Julien Morin[2]

[1]*Institut Lumière Matière, Université Lyon 1 & CNRS, Lyon, France, amanda.ross@univ-lyon1.fr* [2]*Laboratoire Univers et Particules de Montpellier, Universite ́ Montpellier 2, France, julien.morin@umontpellier.fr*

We examine the magnetic response of $A^6\Sigma^+ – X\ {}^6\Sigma^+$ transitions in CrH, in fields up to 0.5 Tesla, focusing on the strong dissymmetry between σ^+ and σ^- transitions, observed (as predicted)[1] at modest magnetic field strengths. These 'Stokes V' signals can provide a sensitive probe of stellar magnetism in telescope spectropolarimetry : CrH (and FeH) feature prominently in spectra of cool dwarf stars. Direct Stokes-V measurements are made in the laboratory with a rotating quarter-wave plate, using lock-in amplification detection at 2f to generate $(\sigma^+ - \sigma^-)$ signals.

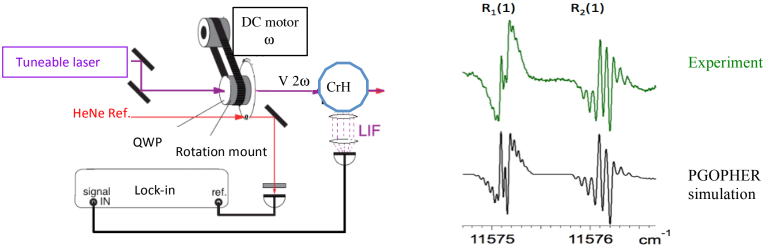

Fig 1. Schematic view of experiment, and illustration of Stokes V profile in R(1) lines

Field-free line positions are known[2-4] for the 760 and 870 nm bands of the *A*–*X* system. Infrared LMR studies[5] provide $X\ {}^6\Sigma^+$ state Landé factors, but the Zeeman effect has been observed for only the lowest rotational levels $A^6\Sigma^+$, under molecular beam conditions[6]. We record laser-induced fluorescence spectra using circularly polarised light with a sputter source producing CrH at ~500 K, to extend to higher rotational levels.

Acknowledgements This work was funded by the CSAA Commission Spécalisée d'Astronomie et Astrophysique (INSU/CNRS, France) in 2018.

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Title: High-resolution Astrophysical Mid-IR Observations of SiO and metal oxides in the molecular layer around the variable Chi Cyg

Guido W. Fuchs[1], Eileen Döring[1], Daniel Witsch[1], Thomas F. Giesen[1], John H. Lacy[2], Rohini S. Giles[3] and Thomas K. Greathouse[3]

[1] Laboratory Astrophysics, University of Kassel, Germany. Corresponding author: fuchs@physik.uni-kassel.de, [2] Department of Astronomy, University of Texas at Austin, USA, [3] Space Science Department, Southwest Research Institute, USA.

The Mira-type variable Chi Cyg is an old asymptotic S-type giant branch (AGB) star that expels large amounts of material into space. This material forms dust and small to intermediate sized molecules - especially molecules composed of refractory materials. It is assumed that molecules like TiO and other small metal oxides that are formed in the expanding stellar atmosphere play a key role in the darkening process during the stellar pulsation.

At temperatures around 1000 K the maximum radiation is shifted to the mid-infrared region, where laboratory spectroscopic data of small metal oxide molecules are sparse. To overcome the lack of data we have recently studied the molecules TiO, Al_2O and VO in the Kassel laboratory for astrophysics at high spectral resolution in the mid-infrared (IR) region. In addition, new observations using the TEXES spectrograph on the NASA Infrared Telescope Facility (IRTF) have been performed to investigate this star at high spectral resolution around 8.3 and 10 μm, i.e., at wavelengths were SiO, TiO, and VO have strong vibrational bands. We performed spectral and line shape analysis of SiO to study the dynamical behavior of the molecular layer surrounding the star. Preliminary results concerning TiO in Chi Cyg will be presented.

Toolbox *'Radioactive Molecules'*: An astrochemical perspective

Alexander A. Breier[1], Thomas F. Giesen[1]

[1] *University of Kassel, Institute of Physics, Heinrich-Plett Str. 40, 34132 Kassel, Germany,*
a.breier@physik.uni-kassel.de

Astrophysical observations of radioactive isotopes, like ^{26}Al, ^{44}Ti, or ^{60}Fe, provide insight into the nucleosynthesis of stellar cores[1]. Recently, the radioactive molecule ^{26}AlF was unambiguously astronomically identified towards the object *CK Vul* [2] by rotational transitions in the microwave spectral region, using the radio telescope observatory ALMA and other telescope facilities. In addition, the vibrational modes of radioactive molecules can be used to identify them in hot stellar environments with infrared instruments such as EXES/SOFIA or the James Webb telescope.
While accurate rotational and vibrational spectra of diatomic molecules can be derived from laboratory measurements of their stable isotopologues, this isotopic scaling method fails for triatomic species such as ^{26}AlOH and for all larger species and thus, requiring in situ spectroscopic measurements on radioactive molecules. Facilities such as ISOLDE/CERN [3] and TRIUMF in Canada are perfectly suited for producing radioactive molecules in supersonic beams. Spectroscopic studies of radioactive species at ISOLDE or TRIUMF will enable future astronomical observations that will provide more detailed information about the processes in the interiors of massive stars. In this talk, astrophysically relevant molecules for studies using rotational and vibrational spectroscopy will be discussed.

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Rotationally Resolved Spectroscopy for Interstellar Chemistry – The cyanonaphthalenes.

Don McNaughton[1], **Michaela K. Jahn[2], Michael J. Travers[2], Dennis Wachsmuth[2], Peter D. Godfrey[1] and Jens-Uwe Grabow[2]**

[1] School of Chemistry, Monash University, Clayton, Victoria, Australia 3800; [2] Institut für Physikalische Chemie and Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität, Lehrgebiet A, Callinstraße 3A, D-30167 Hannover, Germany.

Much of the direct knowledge of interstellar chemistry arises from the powerful combination of radio and mmwave telescopes, rotational resolved spectroscopy and computational and theoretical modelling. Over the last 50 years developments in each of these scientific disciplines has resulted in the identification of around 270 molecules in the interstellar medium or circumstellar shells. A number of example chemical systems from cm-wave, mm-wave will be explored to outline these developments.

Propadienone: Is the heavy atom chain bent or linear and why despite being the lowest in energy, is it the only one of three C_3H_2O isomers not detected in the ISM?

Glycine has many conformers, none of which has yet been detected in the ISM despite a number of searches and a raft of computational studies.

Cyano-substituted molecules: The cyano group is ubiquitous in the molecules detected in the ISM primarily because it provides a large dipole moment leading to strong signals. The largest ISM molecules apart from C_{60} and C_{70} are the long chain cyanopolyynes. We recently assigned the rotational spectra of the four cyano substituted polycyclic aromatic hydrocarbon (PAH) molecules 1-cyanonaphthalene, 2-cyanonaphthalene, 9-cyanoanthracene, and 9-cyanophenanthrene[1] to provide data for an interstellar search. In 2021 the McGuire group successfully located both cyanonaphthalenes in the Tauras molecular cloud[2].

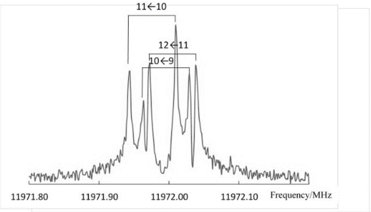

Fig 1, $11_{2,10} \leftarrow 10_{2,9}$ *transition of 2 cyanonaphthalene from ref 1.*

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Disentangling magnetic dipole and electric quadrupole contributions in the spectra of molecular oxygen at 1.27 µm

Iouli Gordon[1], Didier Mondelain[2], Samir Kassi[2], Alain Campargue[2], Helene Fleurbaey[2,3], David Long[3], Joseph Hodges[3]

[1]Center for Astrophysics | Harvard & Smithsonian, USA, igordon@cfa.harvard.edu; [2], CNRS, LIPhy, Université Grenoble Alpes, France; [3]National Institute of Standards and Technology, USA

The $a^1\Delta_g - X\,^3\Sigma_g^-$ band of O_2 at 1.27 µm is very important for atmospheric applications. It is employed for benchmarking by the Total Carbon Cycle Observing Network (TCCON) and will be used for the same purposes by MicroCarb and MethaneSAT missions. It is therefore essential to have spectroscopic reference data allowing retrievals on a sub-percent level of accuracy. However, the spectroscopy of this band is not trivial at this level as the transitions with $\Delta J=0, \pm1$ have both magnetic dipole (M1) and electric quadrupole (E2) contributions. These contributions have different rotational distributions of intensities within the branches, making modeling even harder. In addition, the intensities of the quadrupole branches largely depend on which spin component of the ground state is involved, as intensities are enhanced through the mixing of these components with different high-lying electronic states. Here we make use of the accurate CRDS measurements of the M1+E2 intensities of $\Delta J=0, \pm1$ transitions at NIST [1] and Grenoble ([2] with some additional data taken more recently). In addition, new measurements of $\Delta J=\pm2$ E2 transitions in Grenoble were carried out, accessing all allowed branches, including the very weak *O(N)O(J)* and *S(N)S(J)* branches which allow for direct evaluation of the contribution of mixing of the ground electronic state with a $^1\Pi$ state located at about 60000 cm^{-1} above. Thanks to these measurements we were able to substantially advance the modeling of the rovibronic intensities in the $a^1\Delta_g - X\,^3\Sigma_g^-$ band of O_2, including accounting for very weak interactions with high-lying electronic states and empirical Hermann-Wallis-like corrections. The model allows for the reproduction of best intensity measurements within small fractions of a percent.

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Line parameter measurements in the mid-infrared region using a high-resolution quantum cascade laser dual-comb spectrometer in step-sweep mode

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

[1]Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, Belgium, muriel.lepere@unamur.be; [2]IRsweep AG, Stäfa, Switzerland, jakob.hayden@irsweep.com, pitt.allmendinger@irsweep.com, andreas.hugi@irsweep.com, markus.mangold@irsweep.com

The increasingly accurate measurement of line parameters for a large number of molecules is one of the major challenges of high-resolution molecular spectroscopy. It is indeed crucial for the understanding of intra- and inter-molecular interactions and atmospheric retrievals. The improvements made in recent years in both state-of-the-art theoretical models and in on-board spectrometers for atmospheric studies challenge laboratory measurements.

For a long time, Fourier transform and laser-based spectroscopies were used for studies of infrared absorption line parameters such as the absolute intensity, collisional broadening and pressure-shift of lines. The recent development of dual-comb spectroscopy at high-resolution makes this technique a powerful tool for this kind of study. We recently reported on the characterization of IRis-F1, our mid-infrared quantum cascade laser based dual-comb spectrometer, in the newly developed step-sweep mode[1,2], which allows high-resolution measurements with a very accurate knowledge of the wavenumber axis. We record complete spectra covering over 50 cm^{-1} in 20 minutes with a frequency accuracy of below 0.0004 cm^{-1} in separately calibrated measurements and below 0.00012 cm^{-1} when the calibration is simultaneous with the sample measurement. In addition, measurements of the Doppler-limited line-width of methane transitions recorded at room temperature have shown that the apparatus function is negligible (< 0.00005 cm^{-1}). With these characteristics and the transmission noise floor of down to 10^{-3}, the step-sweep technique can be employed for challenging studies in molecular spectroscopy.

We report that IRis-F1 is a powerful tool for accurate measurements of absorption line parameters in the mid-infrared region. This is illustrated by examples of recent studies devoted to methane diluted in nitrogen, nitrous oxide, acetylene and sulfur dioxide.

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Session D

Posters

August 30, Tuesday, 16:20

Microwave Spetroscopy Detection of π-Stacked Naphthalene Dimers: Is Hydrogen Bonding Assisting or Competing with Stacking?

Wenqin Li[1], **Camilla Calabrese**[1], **Rizalina T. Saragi**[1,2], **Marcos Juanes**[1,2], **Cristóbal Pérez**[1], **Alberto Lesarri**[1]

[1]*Departmento de Química Física y Química Inorgánica, Facultad de Ciencias – Instituto CINQUIMA, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid (Spain)*

[2] *Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25/3, 6020, Innsbruck (Austria)*

Wenqin Li: wenqin.li@uva.es; Camilla Calabrese: camilla.calabrese@uva.es; Rizalina T. Saragi: rizalina.saragi@uibk.ac.at; Marcos Juanes: marcos.juanes@uibk.ac.at; Cristóbal Pérez: cristobal.perez@uva.es; Alberto Lesarri: alberto.lesarri@uva.es

π-Stacking interactions play an important role in organic and organometallic synthesis, protein structure and supramolecular Chemistry. However, the observations on π-stacking in gas-phase are rare. In previous works, the homodimers of 1-naphthol [1] (1N-1N) and 2-naphthalenethiol [2] (2NT-2NT) have been detected using chirped-pulse broadband Fourier transform microwave spectroscopy. In the two observed dimers, hydrogen bonding was not observed, and parallel-displaced crossed structures were used to form the two detected clusters. In this work, we examined the non-covalent interactions in the heterodimers formed between 1-naphthol and 1-naphthalenethiol (1N-1NT) and between 2-naphthol and 2-naphthalenethiol (2N-2NT). One isomer was observed for both heterodimers (*Fig. 1*), with cooperative π-π stacking and O-H···S hydrogen bonding interactions. Considering these results, it is debatable why the stronger O-H···O hydrogen bond was not found for 1N-1N. During the conference supporting experimental and computational results on this problem will be offered.

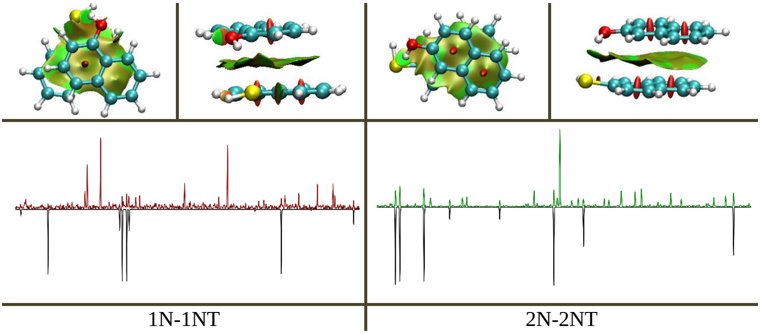

Fig. 1: The observed heterodimers of 1N-1NT (left) and 2N-2NT (right) and a typical microwave spectrum.

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Line models of HCN and HNC in the Interstellar Medium: Perspectives to use machine learning in observational astrochemistry

Edgar Mendoza[1], Miguel Carvajal[1], Jacques Lepine[2], Pietro Dall'Olio[1], Samuel Lopez Dominguez[3], Antonio Peregrín[3], Floris F.S. van der Tak[4], Luciene Coelho[5]

[1]Departamento de Ciencias Integradas, Universidad de Huelva, Spain, edgar.mendoza@dci.uhu.es; [2]Instituto de Astronomia, Geofisica e Ciências Atmosféricas, Universidade de São Paulo, Brazil; [3]Laboratorio de Computación, Universidad de Huelva, Spain; [4]Kapteyn Astronomical Institute, University of Groningen, The Netherlands; [5]Planetário da Universidade Federal de Goiás, Instituto de Estudos Socioambientais, Brazil

In this work, we present results on the line simulation of HCN and HNC in view of applying machine learning methods in astrochemistry, which is a research field continuously fed by data from astronomy, chemistry and physics. As a pilot program, we compute spectra of HCN and HNC since those molecules are broadly used in astrochemistry. To simplify the data and spectral entries, both molecules are fundamentally seen as triatomic species (Fig. 1a), which are chemically associated with the di- and tetratomic species CN and HNCO, respectively. The simulations take into account mechanisms of excitation, isomerization and isotopic fractionation. Line ratios of HCN/DCN, $H^{12}CN/H^{13}CN$ and $HC^{14}N/HC^{15}N$ are analysed, as well as the HCN/HNC balance to constrain interstellar isomerization via

$$HCNH^+ + e^- \rightarrow HCN + H,$$
$$HCNH^+ + e^- \rightarrow HNC + H,$$

we also revise the channel

$$HNCO + C \rightarrow CO + HNC,$$

as a function of different temperature values (e.g. partition functions) in the ISM [1,2]. In perspective, the dataset generated here (Fig. 1b) will be tested in operations of spectral identification and observing time calculation in facilities such as the Large Latin American Millimeter Array (LLAMA).

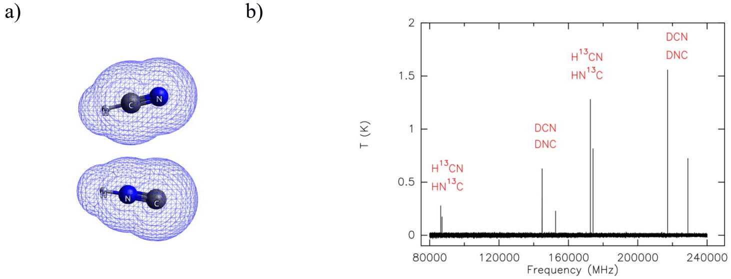

Fig. 1: a) Chemical structures of the triatomic molecules hydrogen cyanide and hydrogen isocyanide HCN and HNC, respectively. b) Computed spectra of the isomers $H^{13}CN$ and DCN, and $HN^{13}C$ and DNC.

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Magnetic response of FeH : the e $^6\Pi$- a $^6\Delta$ system

Amanda Ross[1], **Patrick Crozet**[1], **Allan G. Adam**[2], **Dennis W. Tokaryk**[3]

[1]Institut Lumière Matière, Université Lyon 1 & CNRS, Lyon, France, amanda.ross@univ-lyon1.fr and patrick.crozet@univ-lyon1.fr ; [2]Chemistry Department, University of New Brunswick, Fredericton NB, Canada agadam@unb.ca [3]Physics Department, University of New Brunswick, Fredericton NB, Canada, dtokaryk@unb.ca

We present preliminary results of investigations of the Zeeman splittings seen in low-J lines of the green systems of FeH originating from excited electronic states. FeH is prepared in a chemiluminescent flame, reacting iron pentacarbonyl with atomic H in a flow of argon, as described by Beaton et al.[1] A cw dye laser (Coumarin 521 dye) was tuned to known resonances in the e-a system.[2] Doppler-limited excitation spectra were recorded with and without a magnetic circuit surrounding the intersection between laser beam and molecular plume; the laser's linear polarisation axis was perpendicular to the direction of the magnetic field. Fields up to 0.45 T were achieved with NdFeB magnets. The strongest fluorescence signals (LIF) were also recorded on a Fourier transform spectrometer, giving simultaneously $\Delta M_J = 0, \pm 1$, to v=0 and v=1 of the lowest spin components of the a $^6\Delta$ state, retaining partial $M_{J'}$ selectivity.

The two lowest rotational levels of A $^4\Pi$ have been identified in our spectra so far. The observations are significant because the low-lying A $^4\Pi$ state is the lower state in strong IR bands seen in absorption spectra of cool stars. The determination of effective Landé factors for A $^4\Pi$ will be critical for the interpretation of telescope polarimetric data.[3]

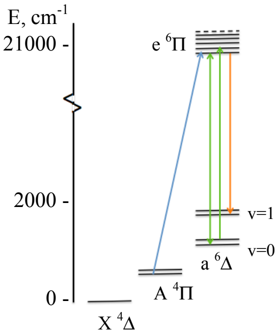

Fig. 1: Low-lying electronic states of FeH.

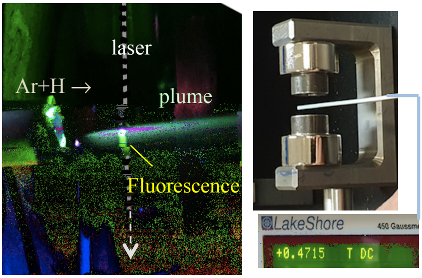

Fig 2 : Photos of LIF and magnetic circuit.

Acknowledgements

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Accurate spectroscopy of molecular hydrogen: hyperfine structure and magic wavelength for a rovibrational transition

H. Jóźwiak[1], P. Wcisło[1]

[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics,
Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Toruń, Poland

Molecular hydrogen, among other simple calculable atomic and molecular systems, possesses a huge advantage of having a set of ultralong living rovibrational states that make it well suited for studying fundamental physics and testing quantum theory. Frequencies of rovibrational transitions in the ground electronic state of molecular hydrogen are now measured with remarkable accuracy, with uncertainties reaching a sub-parts-per-billion level.[1] At this level of accuracy, hyperfine interactions, originating from magnetic and electric multipole moments of the nuclei, should be taken into account in the experimental analysis.

We present the study of the hyperfine structure of the six isotopologues of hydrogen: H_2, HD, D_2, HT, DT and T_2. We provide positions and intensities of all electric dipole and quadrupole rovibrational transitions within the ground electronic $X^1\Sigma$ state.[2] We analyze the leading interactions which determine the hyperfine splitting of the two excited electronic states: the double-well $EF^1\Sigma$ state, and the $B^1\Sigma$ state.[3] The results obtained for the excited electronic states are important for the multiphoton spectroscopy of molecular hydrogen, which is used to determine the dissociation energy, the frequency of the fundamental vibrational splitting, and the energy interval between *ortho* and *para*-H_2.[4]

The accuracy of experimental studies of molecular hydrogen depends on the approach used. For molecular beam experiments, the most important factor contributing to the final uncertainty is the residual first-order Doppler shift.[1] To maintain the progress in accurate metrology, a cold H_2 sample will have to be trapped in an optical lattice. However, since the isotropic dipole polarizability in the v=0 and v=1 vibrational levels of H_2 differs by almost 10%,[5] enormous light shift will dominate the uncertainty budget for the determination of the transition frequency. We find a rovibrational transition for which the AC Stark shift is largely compensated by the interplay between the isotropic and anisotropic components of dipole polarizability. The residual AC Stark shift can be completely eliminated by tuning the trapping laser to a specific “magic wavelength” at which the weak quadrupole polarizability cancels the residual dipole polarizability.

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The water vapour selective absorption spectrum in the 8040-8630 cm^{-1} range

Aleksandra O. Koroleva[1]**, Semen N. Mikhailenko**[2]**, Samir Kassi**[1]**, Alain Campargue**[1]

[1]*LIPhy, Université de Grenoble Alpes, France; aleksandra.koroleva@univ-grenoble-alpes.fr;*
[2]*V.E. Zuev Institute of Atmospheric Optics SB RAS, Russia*

The 1.25 μm transparency window is of importance for a number of atmospheric applications. As a continuation of our previous work on the improvement of water vapour resonance spectrum line parameters in this spectral range [1], the room temperature absorption spectrum of water vapour in natural isotopic abundance was recorded with an unprecedented sensitivity between 8040 - 8620 cm^{-1} using comb referenced cavity ring-down spectroscopy technique [2]. The line positions and intensities of more than 5700 lines were retrieved within the 3.9×10^{-30} - 1.5×10^{-22} cm/molecule intensity range. The assignments were performed using known experimental energy levels and calculated spectra based on variational calculations by Schwenke and Partridge. The final line list contains more than 8300 transitions of six water isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$ and $HD^{17}O$). The high sensitivity and low noise level of about $\alpha_{min}\approx10^{-11}$ cm^{-1} allows detecting a high number of new lines and determine their positions with an accuracy of about 10^{-4} cm^{-1} in the case of isolated lines. Observed line positions allow to found about 70 new energies of three isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$ and $HD^{16}O$) and to correct more than 60 previously reported term values of four isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and $HD^{16}O$).

An overall good agreement of experimental line parameters with line parameters from HITRAN2020 [3] and W2020 [4] is observed. But some deviations are found with amplitude largely exceeding the claimed uncertainty on the W2020 transition frequencies.

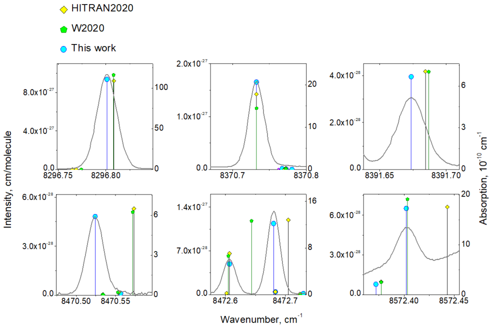

Fig. 1: The examples of deviations between experimental, HITRAN2020 and W2020 data.

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Investigation of the hyperfine structure of the $c^3\Sigma^+$ state in KRb

Velizar R. Stoyanov[1]**, Asen E. Pashov**[2]

[1] *Sofia University "St. Kliment Ohridski", Bulgaria, vstoyanov38@gmail.com;* [2] *Sofia University "St. Kliment Ohridski", Bulgaria*

The study of the hyperfine structure (HFS) in electronic transitions in diatomic molecules is a challenging task due to its experimental and theoretical complexity. We want to study the HFS of one of the $c^3\Sigma^+$ excited states of the KRb molecule, because previous studies indicated that the splitting may be much larger than in similar alkali metal diatomics[1]. Another motivation is that the $c^3\Sigma^+$ state serves as an intermediate state for transferring cold Feshbach molecules from the $a^3\Sigma^+$ state to the ground $X^1\Sigma^+$ state[2]. Due to the proximity of the $B^1\Pi$ state, perturbations caused by the spin-orbit interaction are observed. This makes possible to observe transition to the mixed pair of states from the singlet $X^1\Sigma^+$ state.

We report on the experimental setup for observation of hyperfine structure of the $X^1\Sigma^+$ - ($c^3\Sigma^+$,$B^1\Pi$) transition. Single laser saturation spectroscopy and also optical-optical double resonance saturation spectroscopy in V configuration is used. The obtained experimental results will be presented at the conference.

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Infrared-Millimetre Wave Double-Resonance (IR-mmW-DR):

A comparison of cw-IR/mmW absorption detection and IR-triggered/CPmmWFT detection

Jan Jakob, **Jonas Bosmann, Pascal Stahl, Matin A. Kaufmann,**
Thomas F. Giesen

University of Kassel – Laboratory Astrophysics, Germany, jan.jakob@uni-kassel.de

Double resonance, i.e. applying radiation of two different frequencies simultaneously - in this case infrared (IR) and millimetre wave (mmW) radiation - offers great spectroscopic opportunities. These opportunities range from deciphering ro-vibrational spectra, i.e. assisting line assignments in dense spectra[1,2] to obtaining high-resolution data of excited vibrational states, i.e. precise rotational parameters. The latter is possible due to the high selectivity provided by the IR pumping compared to non-selectively heating the probe to achieve vibrational excitation.

We demonstrate two different approaches, both on two different setups. In either case, the mmW is used to measure rotational transitions while an IR laser alters the molecule's population densities from the thermal equilibrium. In case one, both IR and mmW operate in continuous wave (CW) mode and pure absorption is detected. In case two a mmW chirped pulse (CP) induces a free induction decay (FID) after the IR excitation, similar to developments by Nakajima et al.[3].

For both setups, we have obtained significant changes in population densities of the vibrational ground state as well as pure-rotational spectra in the vibrationally excited state which are only detectable with prior IR excitation.

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Enhancing enantiomer-selective population enrichment by depleting the thermal population

Himanshi Singh[1,2], **Freya E. L. Berggotz**[1,3], **Wenhao Sun**[1], **Cristobal Pérez**[4], **Melanie Schnell**[1,2]

[1]*Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany, himanshi.singh@desy.de, freya.berggoetz@desy.de, wenhao.sun@desy.de, melanie.schnell@desy.de;* [2]*Christian-Albrechts-Universität zu Kiel, Kiel, Germany;* [3]*University of Hamburg, Hamburg, Germany;* [4]*University of Valladolid, Valladolid, Spain, cristobal.perez@uva.es*

Chirality plays a fundamental role in biochemistry as most biomolecules are chiral in nature, i.e., they have preferred handedness encoded in them. The two-handedness of a chiral molecule referred to as enantiomers have identical physical properties, however, due to stereoselective bias, they may have different biochemical and chemical functionalities. To understand these enantiomers functionalities, it is important to determine their handedness and enantiomeric excess.

Most recently, microwave three-wave mixing technique [1] has emerged as a new chiral-sensitive method for studying chiral molecules in the gas phase. The technique was then extended by applying tailored microwave fields to achieve enantiomer-selective population enrichment in a chosen rotational state. [2–5] However, the thermal population and spatial degeneracy (M-states) of the rotational levels limit this enrichment. In this study, we use trifluoromethyl oxirane as a model molecule to demonstrate the enhancement of the enantiomer-specific enrichment by depleting the initial thermal population at the relevant rotational level with a pi-pulse or a fast chirp in the rapid adiabatic passage regime. The effects of both pulses on enantiomer-selective population enrichment will be discussed along with the theoretical simulations.

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Extended laboratory investigation of the pure rotational spectra of CH_2CN, CH_3O and CH_2OH radical species in the millimeter-wave region (up to 900 GHz)

Olivia Chitarra[1], Jean-Thibault Spaniol[1], Thomas Hearne[1], Jean-Christophe Loison[2], Marie-Aline Martin-Drumel[1] and Olivier Pirali[1]

[1] Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, Orsay France; [2] Institut des Sciences Moléculaires (ISM), CNRS, Univ. Bordeaux, 33400 Talence, France

Radical species are suspected to be involved in gas phase reactions occurring in the interstellar medium (ISM) and their detection would give important insights about the chemistry happening in the ISM. To support the search of those molecules, laboratory spectroscopy is essential.

We led new high-resolution studies in the submillimeter-wave region on 3 different radicals: the cyanomethyl (CH_2CN), the methoxy (CH_3O), and the hydroxymethyl (CH_2OH) radicals from 140 GHz up to 900 GHz (millimeter-wave region). These species were produced by H abstraction from their precursor (acetonitrile, CH_3CN, and methanol, CH_3OH) using F atoms. Their pure rotational spectra were recorded using a frequency multiplication chain spectrometer[1].

For those three species, previous investigations only measured transitions up to about 400 GHz[2,3,4] and even allowed for the detection of CH_2CN and CH_3O in the ISM. We completed the spectroscopic characterization above 400 GHz yielding to an improvement in their spectroscopic parameters. The interstellar search for these species can now be undertaken in cold to warn environments of the ISM up to 900 GHz.

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Pure rotational spectra of chlorofluoro-substituted acetonitrile, ethanol and ethyl acetate

Wenhao Sun[1], and Melanie Schnell[1,2]

[1]Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany; [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 1, 24118 Kiel, Germany

Chirality plays a fundamental role in (bio)chemical processes. However, there are still many mysteries waiting to be unravelled, such as the origin of the homochirality of life. To gain a better understanding of chirality at the molecular level, various techniques are developed to study the chiroptical effects of chiral molecular systems. The chloro- and fluoro-substitutions in the methyl group of acetonitrile, ethanol, and ethyl acetate, respectively, turns them into chiral molecules, which attracts our attention.

In this work, we investigate the geometrical and conformational configurations of these chlorofluoro- (ClF-) substituted compounds in their ground vibrational state by combining microwave spectroscopy and quantum-chemical calculations. Their rotational spectra in the frequency range of 18 – 26 GHz were individually measured on our segmented chirped pulse Fourier transform microwave (CP-FTMW) spectrometer. Multiple conformers have been identified in the spectra with the nuclear quadrupole splittings arising from ^{35}Cl ($I = 3/2$) or ^{37}Cl ($I = 3/2$) for ClF-ethanol and ClF-ethyl acetate, which is supported by theoretical calculations.

Linear unsaturated carbon chains observed in the electrical discharge of aromatic molecules.

Donatella Loru[1], Amanda L. Steber[1], Eva Gougoula[1], Gayatri Batra[1], and Melanie Schnell[1,2]

[1]Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany; [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 1, 24118 Kiel, Germany

To date, more than 260 molecules have been identified in the interstellar and circumstellar medium by astronomical observations. Among these molecules, linear unsaturated carbon chains featuring alternating single and triple bonds are one of the dominant structural motifs. The TMC-1 molecular cloud, possibly the nearest star forming region to us, is known to be a rich source of these molecules. The presence of cyclic aromatic molecules in the same cloud was also revealed by recent astronomical detections of cyanobenzene (C_6H_5CN)[1], the two isomers of cyanocyclopentadiene (C_5H_5CN)[2], cyclopentadiene (C_5H_6)[3], the two cyano-functionalized isomers of naphthalene ($C_{10}H_7CN$)[4], and the first pure polycyclic aromatic hydrocarbon indene (C_9H_8)[3,5].

In this work, we have investigated the potential link between highly unsaturated carbon chains and cyclic aromatic molecules by performing electrical discharge experiments of several aromatic molecules featuring a different number of aromatic rings, e.g., phenanthrene ($C_{14}H_{10}$), both pure and in mixture with acetonitrile (CH_3CN), and pyrene ($C_{16}H_{10}$), as well as nitrogen-containing aromatic molecules, e.g., pyrrole (C_4H_4NH), indole (C_8H_7N), and phenanthridine ($C_{13}H_9N$). The resulting products were probed using chirped-pulse Fourier transform microwave spectroscopy in the 2-12 GHz frequency range.

In all the experiments, highly unsaturated hydrocarbon molecules, including cyanopolyynes (HC_nN) and acetylenic free radicals (C_nH), are found to be the predominant discharge products. The formation of cyanopolyynes in the discharge of phenanthrene and acetonitrile was unraveled by isotopic tagging.

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Data for infrared ammonia spectra: Accuracy tests around 6000 cm^{-1}

Ondřej Votava[1], Peter Čermák[2], Jozef Rakovský[1], Patrice Cacciani[3], Jean Cosléou[3],

[1]Heyrovský Institute of Physical Chemistry, Dolejškova 2155/3, Prague 8, 18223, Czech Republic, ondrej.votava@jh-inst.cas.cz; [2]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovakia; [2]Heyrovský Institute of Physical Chemistry, Dolejškova 2155/3, Prague 8, 18223, Czech Republic; [3]Laboratoire de Physique des Lasers, Atomes et Molécules, CNRS, UMR 8523 Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France; [4]UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France; [5]SQUARES, Université Libre de Bruxelles, Brussels, Belgium

Accurate reference laboratory data represents a key element for understanding any remote observations in particular astrophysical surveys. In the current contribution we focus on the accuracy check of our previously published peaklist in the 6000 cm^{-1} region [1]. This comprises two complementary studies. First, the line center validation was performed by the referenced supersonic jet expansion spectra, and second, the multi-temperature analysis focused on the line intensity validation.

The jet spectra were measured in the 5980 and 6090 cm^{-1} range together with reference methane lines. These were recently recorded using the comb coherence-transfer and cavity ring-down saturation spectroscopy in the same region [2]. This analysis yielded frequency accuracy on the kHz level. In the current work we used a frequency stable zerodur étalon to transfer this accuracy to the nearby ammonia lines. At the end a list of 70 lines was produced with the line positions better than 0.0005 cm^{-1} for strong lines.

The multi-temperature analysis was performed in our cryogenically cooled Herriot cell with the same ECDL source used for jet measurements in a small one wavenumber wide range. The idea was to benefit from the measurement at low temperatures where the pressure follows the saturated vapor pressure curve [3] and is thus governed by the temperature. A set of five transitions was studied in the temperature span from 140 K up to room temperature. The measured dependence allowed to check for line intensity consistency of studied lines. Further analysis is in progress to retrieve the accurate values for absolute line intensities as well.

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Resonant-Multi-Photon-Excitation and ToF-MS for Precision Spectroscopy of Astrophysical Molecules

Varazdat Grigorian[1], Matin A. Kaufmann[2], Karel J. Vávra[3], Thomas F. Giesen[4]

[1]University of Kassel, Germany, va.grigorian@gmail.com; [2]University of Kassel, Germany, m.kaufmann@physik.uni-kassel.de; [3]UCT Prague, Czech Republic, karel.j.vavra@gmail.com; [4]University of Kassel, Germany, t.giesen@uni-kassel.de

The molecular composition of diffuse interstellar matter is a century old unsolved problem in astrophysics. Diffuse interstellar bands (DIBs) in the visible spectral range can be observed along many sight lines, however, their carriers are largely unknown. A breakthrough was achieved in 2015 with the assignment of C_{60}^+ as the first identified carrier of DIBs[1]. Yet, the majority of these signals remain unassigned due to the lack of laboratory data. Complex organic hydrocarbons such as polycyclic aromatic hydrocarbons, their ions, or radicals amongst others constitute potential carriers of the DIBs. In an effort to contribute to the spectral data of these molecular species, resonant-multi-photon ionization (REMPI) of gasphase molecules in a molecular beam can be employed and combined with a time-of-flight mass spectrometer (ToF-MS) as a detection method. This instrument provides mass separated spectra with high sensitivity, due to state selective ionization when using multiple photons of different color. The high spectral resolution of this instrument enables the measurement of ro-vibrational transitions of unknown molecular species created in a discharge plasma.

Here, we demonstrate the current state of the experimental setup to observe single ro-vibronic transitions of molecules in a molecular beam with the example of ammonia (NH3).

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Characterizing the class of para-substituted anisole derivatives by high-resolution rotational spectroscopy

M. Li[1], P. Buschmann[1], K. G. Lengsfeld[1], J.-U. Grabow[1]

[1] Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Hannover 30167, Germany
M. Li: meng.li@pci.uni-hannover.de; P. Buschmann: philipp.buschmann@pci.uni-hannover.de
K. G. Lengsfeld: kevin.lengsfeld@pci.uni-hannover.de; J.-U. Grabow: jens-uwe.grabow@pci.uni-hannover.de

In the case of the parent compound anisole [1], until now, the precise values of the barrier to internal rotation could be obtained only for the three cases of 4-anisaldehyde [2], 2-methoxypyridine [3] and 2,6-dimethylanisole [4]. To know more information about the V_3 barriers, some of para-substituted anisole derivatives were investigated by high resolution Fourier transform microwave spectroscopy. The assignments of the recorded signals in the majority of cases were based on the quadrupolar couplings, respectively, which are considerably sensitive to the electronic environment of the nucleus. Thus, the hyperfine structure in the spectrum can serve as an indicator for substitution effects, as in comparable cases [5]. But for present works, also no splittings causing by methyl group internal rotation were observed due to the high V_3 barriers. The influences of different halogen atoms or groups on the V_3 barriers of the methyl internal rotation could be revealed after more measurements and comparisons in the next works.

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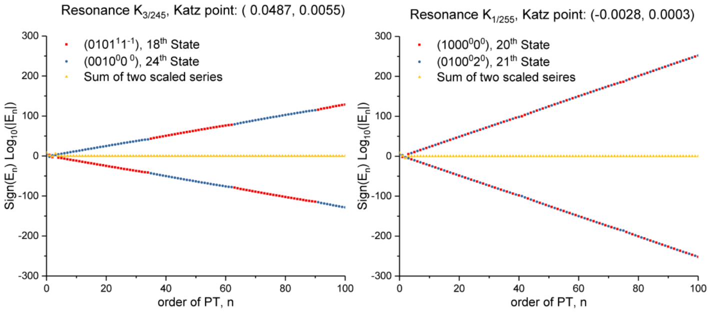
Vibrational resonance analysis of acetylene using the large order perturbation series and Pade-Hermite approximant

Xuanhao Chang[1], Egor O. Dobrolyubov[1], Sergey V. Krasnoshchekov[1]

[1]Department of Chemistry, Lomonosov Moscow State University,
Russian Federation, chang@phys.chem.msu.ru;

The large order Rayleigh-Schrödinger perturbation theory (RSPT) and the quartic Pade-Hermite approximant (PHA) was used for studying the resonance structure of the linear molecule acetylene, combined with an ab initio quartic force field at the level CCSD(T).[1,2] Large order perturbation series of certain vibrational states, calculated by the advanced recursive RSPT formula for a degenerate case, demonstrate strong divergence behaviours and regular anti-sign patterns, indicating the existence of strong couplings between corresponding states in the molecule (fig.1). Such patterns are well controlled by the singularities of the eigenvalues on the complex plane through the Darboux and the Katz theorems, and are further confirmed from the singular points analysis followed by a resummation procedure using a quartic Pade-Hermite approximant.

As the result, all classical resonances, including the stretching Darling-Dennison coupling, three stretch-bend couplings and the bending Darling-Dennison coupling, were confirmed by the applied method. Two interpolyad resonances, proposed by Herman et.al.,[3] were supported by our calculation. In addition, we proposed an independent new interpolyad resonance $K_{2/4444}$. The complete analysis of the RSPT series and their singularities provides a comprehensive resonance structure of the acetylene.



(a) (b)

Fig. 1: The selected RSPT series of vibrational states:

(a) $\nu_2+\nu_4+\nu_5$ and ν_3; (b) ν_1 and $\nu_2+2\nu_5$.

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Resonance and Polyads of Carbonyl Sulphide (OCS) Isotopologues Studied by Padé-Hermite Resummation of Divergent RSPT Series

Egor O. Dobrolyubov[1], Xuankhao Chang[1], Sergey V. Krasnoshchekov[1]

[1]*Dept. of Chemistry, Lomonosov Moscow State University, Russian Federation,*
chang@phys.chem.msu.ru

A presence of vibrational cubic Fermi and quartic Darling-Dennison resonances in a molecule requires the inclusion of the corresponding resonance terms in the form of the effective Hamiltonians describing a certain spectral range. There are several ways of detecting such resonances, both by ab initio theoretical methods and experimentally, using various techniques. The vast majority of all these approaches have a significant portion of uncertainty in dealing with weaker resonances. In other words, while theoretical methods rely on somewhat empirical criteria,[1-2] experimental methods also depend on certain human choices. In a wider context, a reliable knowledge of all resonances defines the form of a polyad quantum number.

A fundamental method of studying vibrational resonances can be established by combining the Rayleigh-Schrödinger perturbation theory (RSPT) with a subsequent procedure of representing typically divergent large order vibrational energy series by multivalued Padé-Hermite approximants (PHA). So far, a number of such studies were accomplished on non-linear molecules.[3-4] In this work we extend this method to a few isotopologues of a three-atomic linear molecule OCS.

The ab initio vibrational Watson Hamiltonian with Sayvetz condition is used to formulate purely vibrational problem. Large order (~200) RSPT series are calculated for vibrational states up to 12-th polyad. Obtained series are treated by quartic PHA and their critical points were found as discriminant roots. According to Katz theorem, a pair of matrix eigenvalues may be connected by Hermitian conjugate complex critical points. The definitive condition of a resonance case can be formulated as a location of critical points within a unit circle on the complex plane. Moreover, non-principal branches of quartic approximants often coincide with other nearby resonant states.

In conclusion, the OCS literature resonances $(0,4^0,-1)$ and $(1,-2^0,0)$ are acknowledged,[5] in accord with the polyad form (2,4,1).[6] Moreover, the presence of a weaker interpolyad resonance $(5,0^0,-2)$ is theoretically found as well, approving the experimental observations in vibration-rotation spectra.[7]

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Recent analysis of high-absorption path FT spectra of acetylene

David Jacquemart[1], **Oleg M. Lyulin**[2], **Aleksander M. Solodov**[3], **Tatiana M. Petrova**[4], **Alexandr A. Solodov**[5]

[1] Sorbonne Université, CNRS, MONARIS, France, david.jacquemart@sorbonne-universite.fr; [2] V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Russia, ol@iao.ru; [3] V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Russia, solodov@iao.ru; [4] V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Russia, tanja@iao.ru; [5] V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Russia, asolodov@iao.ru

Recent acetylene spectra have been recorded at the V.E. Zuev Institute of Atmospheric Optics SB RAS from IAO (Tomsk) with a Bruker IFS-125HR Fourier transform spectrometer connected to a White type cell (absorption paths length up to 1057.95 m). The Bruker resolution is ranging from 0.005 to 0.016 cm^{-1} depending on studied spectral regions. Acetylene pressures ranging from 1 to 10 mbar have been used. This work is focused on the spectral region between 2400 and 2800 cm^{-1} where HITRAN and GEISA databases have spectroscopic data for only 5 bands whereas with present experimental spectra more than 20 bands can be observed and were analyzed by a line-by-line multispectrum fitting procedure. Also the *Q*-branch of the $\nu_1+\nu_3+3\nu_4$ cold band of $^{12}C_2H_2$ located at 8330 cm^{-1} was considered since this strong *Q*-branch is missing from spectroscopic databases. These works complete the recent updates of acetylene in HITRAN and GEISA both in the $\Delta P = 4$ (previous update in 2008) and $\Delta P = 13$ (previous update in 2020) spectral regions.

The ν_3 band of $^{16}O^{14}N^{18}O$: line positions and intensities

Anastasia A. Marinina [1], David Jacquemart [2], Lahouari Krim [3], Pascale Soulard [4], Valery I. Perevalov [5]

[1] V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Russia, lukashevskaya@iao.ru; [2] Sorbonne Université, CNRS, MONARIS, France, david.jacquemart@sorbonne-universite.fr; [3] Sorbonne Université, CNRS, MONARIS, France, lahouari.krim@sorbonne-universite.fr; [4] Sorbonne Université, CNRS, MONARIS, France, pascale.soulard@sorbonne-universite.fr; [5] V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Russia, vip@iao.ru

The $^{16}O^{14}N^{18}O$ is one of the most abundant daughter isotopologues of nitrogen dioxide. Its natural abundance is about 0.397%. This value is slightly larger than the value of the natural abundance of the $^{15}N^{16}O_2$ isotopologue (0.365%). In Ref. [1] it is shown that the inclusion of the $^{15}N^{16}O_2$ lines to the fitting of the atmospheric balloon spectra significantly reduces the rms spectral fitting residuals in the 1550 – 1650 cm^{-1} region. The addition of $^{16}O^{14}N^{18}O$ isotopologue in databases could improve the gases retrievals from the atmospheric spectra in this region.

Fourier transform IR spectra of samples prepared by mixing two gaseous species $^{18}O_2/^{14}N^{16}O$ (1:2) have been recorded in the region of the ν_3 band of nitrogen dioxide. The spectra contain the lines corresponding to the ν_3 band of the $^{16}O^{14}N^{18}O$ isotopologue within the 1540-1640 cm^{-1}. In total 1795 lines of the ν_3 band of this isotopologue were assigned with the rotational quantum numbers N and K_a up to 51 and 12, respectively, what corresponds to 3487 electron spin-rotation-vibration transitions. The overall measured set of the line positions was used to fit the effective Hamiltonian parameters. The fitted set of the parameters reproduces the observed line positions with an rms of 3.6×10^{-3} cm^{-1}. A selected set of the measured line intensities was used to determine the effective dipole moment parameters describing the line intensities of the ν_3 band. The rms deviation of the fit is 5.0%. It was found that the lines with the $\Delta K_a = \pm1$ are very weak compared to those with the $\Delta K_a = 0$. At attained sensitivity only few lines with the $\Delta K_a = \pm1$ were assigned. A line list of this band has been generated for databases.

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Cantilever-enhanced Photoacoustic Spectroscopy for the Multicomponent Analysis of Gases

Jan Suchánek[1], Michal Dostál[1], Zdeněk Zelinger*[1]

[1]J. Heyrovsky Institute of Physical chemistry Academy of Sciences of the Czech Republic
*Prague, Czech Republic, *corresponding author*

Cantilever-enhanced Photoacoustic Spectroscopy (CEPAS) [1, 2] in combination with wavelength modulation spectroscopy was used for the multicomponent analysis of gases. Distributed feedback Quantum Cascade laser tunable in the region of ~1045 – 1048 cm^{-1} was used as the excitation source. Principal component analysis (PCA) and Partial least squares (PLS) methods were applied to a mixture of selected substances in the gas phase to both simulated (www.spectraplot.com) and experimentally acquired spectra, PCA predicting the number of substances and PLS its concentrations.

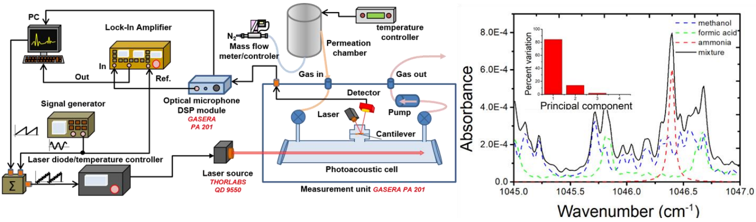

Fig. 1: Experimental design and simulated spectra of methanol (1ppm, blue), formic acid (5 ppm, green), ammonia (0.1 ppm, red) and their mixture (black). Inset – 3 principal components acquired from PCA analysis suggesting three substances in the mixture

Table 1: Concentrations predicted by PLS model applied on the spectra of ethanol/methanol mixtures

	Methanol		Ethanol	
Mixture	Prepared concentration (ppm)	Predicted concentration (ppm)	Prepared concentration (ppm)	Predicted concentration (ppm)
1	2.56	3.1	19	22
2	3.69	4.02	19	19.5
3	1.13	1.33	6.63	7
4	5.19	4.5	40.5	37
5	6.32	5.66	21.5	18.9
6	6.32	5.8	40.5	38.1

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The Higher Hot Torsional Bands (ν=3←1 And ν=4←1) Of Methylamine - Preliminary Analysis

Iwona Gulaczyk, Marek Kręglewski

Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poland, gulai@amu.edu.pl, mkreg@amu.edu.pl

Methylamine is a molecule performing two large amplitude motions: CH_3 internal rotation and NH_2 inversion. These two large amplitude motions are strongly coupled and give rise to a rotation-inversion-torsion structure in the vibrational states. The rovibrational spectrum of the methylamine molecule has been extensively studied both experimentally and theoretically. The analyses of infrared bands such as inversion or CN stretching show significant perturbations from highly excited torsional states. In order to untangle the interactions in the 700-1200 cm^{-1} region of the methylamine spectrum, it is crucial to assign the perturbing states, which are the third and fourth excited torsional states ($3\nu_{15}$ and $4\nu_{15}$).

The spectra were recorded with a resolution of 0.00125 cm^{-1} using Bruker IFS-120HR spectrometer at the University of Oulu.

The accurate energy levels of the first excited torsional state, ν_{15}, [1,2] were used as reference values for Lower State Combination Differences (LSCD) in the assignments of the third and fourth torsional hot bands, ν_{15}-$3\nu_{15}$ and ν_{15}-$4\nu_{15}$. After the complete analysis in the second torsional overtone region (360-720 cm^{-1}) was performed [3], the remaining unassigned lines in this region could be tentatively assigned to ν=3←1 and ν=4←1 bands.

Previously, some transitions belonging to ν=3←1 and ν=4←1 bands have been found and assigned (about 200 transitions of B, E_{1+1} and E_{1-1} symmetry and up to low K values only for the $3\nu_{15}$ and 28 transitions of B symmetry only for $4\nu_{15}$) [4].

On the basis of the calculated energy levels for the third and fourth excited torsional states, many transitions of the hot band ν=3←1, not assigned previously, have been identified (over 1700 transitions for all symmetry species). As for ν=4←1, so far, the previously assigned series were only extended to higher J values (over 100 transitions assigned of B symmetry), but the analysis is in progress. All the assignments were confirmed by the LSCD.

Each set of the experimental data was fit to a single state model based on the group theoretical formalism of Hougen and Ohashi [5]. The standard deviation of 0.015 cm^{-1} was obtained so far for the third excited torsional state. The work is in progress.

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Continuum absorption of CO_2 in the millimeter wavelength range

Aleksandr A. Balashov[1], **Tatyana A. Galanina**[1], **Aleksandra O. Koroleva**[1], **Evgeny A. Serov**[1],
Maksim A. Koshelev[1], **Daniil N. Chistikov**[2,3,4], **Artem A. Finenko**[2,4], **Sergey V. Petrov**[2],
Andrey A. Vigasin[3], **Mikhail Yu. Tretyakov**[1]

[1]Institute of Applied Physics of Russian Academy of Sciences, Russia, balashov@ipfran.ru; [2]Lomonosov Moscow State University, Russia; [3]A.M. Obukhov Institute of Atmospheric Physics, Russia; [4]Irkutsk National Research Technical University, Russia

In the Earth's, Venusian, and Martian atmospheres, carbon dioxide (CO_2) is a strong absorber of infrared radiation, trapping the heat and causing a potent greenhouse effect. Because CO_2 molecules lack a permanent dipole moment, the absorption spectrum in the millimeter wavelength range does not exhibit resonant absorption lines and is dictated solely by continuum absorption of bimolecular origin. We conducted an in-depth investigation of mm-wave absorption in pure CO_2 and its mixture with argon, seeing those systems as prototypes for more intricate scenarios manifesting as continuum-like troughs in between the dipole-permitted rovibrational bands, which is the case, for example, in water vapor. Our desire to develop a well-grounded understanding of the nature of the continuum motivates the joint theoretical and experimental efforts presented here.

The experimental data on the CO_2 continuum in the mm-wave range are limited and based on single frequency point observations with large uncertainties[1]. We extend our previously reported results[2], obtained at room temperature only, by recording the spectra of pure CO_2 and its mixture with Ar using a resonator spectrometer[3] at temperatures between 268 and 317K and varied pressures ranging from 375 to 1490 Torr.

To simulate the collision-induced absorption, we used a semiclassical trajectory-based formalism[4], consistently accounting for the true dimer contribution. The excellent agreement between the simulated and measured CO_2-Ar continuum supports both theoretical and experimental approaches. The frequency dependence of continuum absorption notably deviates from the generally utilized quadratic behavior, which was found to be greatly influenced by both metastable and true dimers. Theoretical values of the CO_2-CO_2 continuum regularly underestimate the observed ones by roughly 20%, which can be tentatively attributed to the assumption of the rigidity of CO_2 molecules. For atmospheric studies, we propose a parameterized model for the frequency and temperature dependence of the CO_2-Ar continuum.

The work is supported by the RSF project 22-17-00041.

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Study of the vibrational structure of symmetric and asymmetric isotopologues of CO_2

Marisol Bermúdez-Montaña[1], Marisol Rodríguez-Arcos[1], Miguel Carvajal [2], Christian Ostertag-Henning [3], Renato Lemus [4]

[1]*Tecnológico de Monterrey, Mexico*

[2]*Centro de Estudios Avanzados en Física, Matemáticas y Computación, Unidad Asociada GIF-MAN, CSIC-UHU, Universidad de Huelva, 21071 Huelva, Spain*

[3]*Federal Institute for Geosciences and Natural Resources, Germany*

[4]*Instituto de Ciencias Nucleares, UNAM. A. P. 70-543, Circuito Exterior, C. U. 04510 Mexico, CDMX, Mexico*

A polyad-preserving algebraic model has been applied to the study of the vibrational excitations of the symmetric and asymmetric isotopologues of carbon dioxide in their electronic ground states[1]. We have analyzed the set of available experimental data for six isotopologues ($^{13}C^{16}O_2$, $^{12}C^{18}O_2$ and $^{12}C^{17}O_2$; and $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, and $^{16}O^{13}C^{18}O$) with results comparable with other variational and *ab initio* calculations[2-6] and, in general, with spectroscopic quality. The approach considers a SU(2) algebra, associated with a Morse oscillator, for each stretching internal coordinate and a U(3) algebra for the bending mode.

This work is an extension of the published studies about the main isotopologue carried out previously[7-11] and aims to simulate the Raman spectra of the six isotopologues with high accuracy.

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Validation of the atmospheric absorption models within 20-60GHz range by simultaneous radiosonde and microwave observations: the advantage of using ECS formalism

D.S. Makarov[1], M.V. Belikovich[1], E.A. Serov[1], M.Yu. Kulikov[1], and A.M. Feigin[1]

[1]*Institute of Applied Physics, Russia, dmak@ipfran.ru;*

The precise calculation of the atmospheric absorption in microwave band is highly important for atmospheric remote sensing with ground-based and satellite-borne radiometers, as it is a key element in procedures for temperature, humidity or trace gas concentration retrieval. The precision of the absorption model directly affects the accuracy of the retrieved information and reliability of the resulting forecasts. In this study, we analyze the difference between observed and simulated brightness temperature (T_b) spectra obtained from more than four years of microwave and radiosonde observations in the range 20-60 GHz. In this range, the wing of the molecular oxygen 60-GHz band contributes significantly to the T_b. Two modelling approaches are compared: line-by-line used in Millimeterwave Propagation Model (MPM), suggesting terms of the 1st and 2nd order of the pressure value[1,2], and Energy Corrected Sudden[2,3] (ECS) one. The use of an absorption model from MPM in simulations leads to a significant difference in frequency channels within the 51-54 GHz range, while the calculations employing a more accurate ECS model reduces the difference several times.

The study is supported by Russian Science Foundation under grant No 18-72-10113, https://rscf.ru/en/project/18-72-10113/.

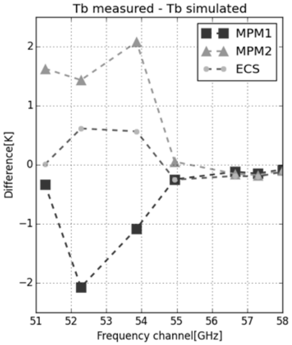

Fig. 1: Difference between measured brightness temperature T_b and one simulated using various approaches to the modeling of the molecular oxygen 60-GHz band.

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Temperature behaviour of the molecular oxygen fine structure lines speed-dependent parameters

D.S. Makarov[1], **M.A. Koshelev**[1], **G.Yu. Golubyatnikov**[1], **I.N. Vilkov**[1], **T.A. Galanina**[1], **E.A. Serov**[1], **P.W. Rosenkranz**[2] **and M.Yu. Tretyakov**[1]

[1]*Institute of Applied Physics, Russia, dmak@ipfran.ru*;[2]*Massachusetts Institute of Technology, Cambridge, USA*

Fine structure lines of the oxygen molecule are located mostly in the range 50-70 GHz and a single line is at 118 GHz. These lines are widely used in radiometric atmospheric measurements for retrieving the temperature distribution which requires absorption and radiative transfer models. The accuracy of determining the atmospheric parameters depends on the accuracy of the model, in particular, on the underlying spectroscopic parameters of the molecular lines and continuum. This work continues our study of the speed dependence effect and its influence on a shape of the fine structure oxygen lines at various temperatures. Profiles of the lines were recorded using three spectrometers having different operation principles. All instruments employed demonstrate enough sensitivity to observe speed-dependent collisional effects manifestation in the line shape. Using corresponding speed-dependent model profiles with the quadratic dependence of the collisional cross-section on the absorber speed allowed measurement of the collisional broadening parameters γ_0 and γ_2 with their temperature dependencies and rotational behavior of the T-dependence parameters. The obtained data set made it possible to refine significantly the molecular constants responsible for the fine structure of the rotational oxygen levels (the uncertainty was reduced from 4 to 6 times), weak pressure shifts of the line centers are observed for the first time. In addition, for the 1-line mixing parameter *y* and its' temperature dependence was refined with increased accuracy.

The study is supported by Russian Science Foundation under grant No 18-72-10113, https://rscf.ru/en/project/18-72-10113/.

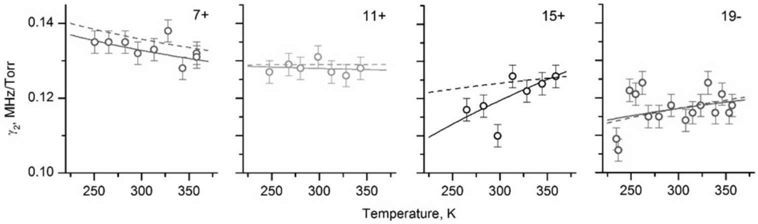

Fig. 1: Temperature behavior of the speed dependence parameter γ_2 for some fine structure lines. Solid lines represent the fitted power law function. Dashed lines demonstrate the empirical T-dependences based on the whole dataset analysis. Error bars are 3σ fit uncertainties.

Millimeter and submillimeter spectroscopy of isobutene and its detection in the G+0.693 molecular cloud

Mariyam Fatima[1], Oliver Zingscheim[1], Víctor M. Rivilla[2], Izaskun Jiménez-Serra[2], Jesús Martín-Pintado[2], Stephan Schlemmer[1]

[1]I. Physikalisches Institut, Universitat zu Köln, Germany, fatima@ph1.uni-koeln.de;
[2]Centro de Astrobiología (CSIC-INTA), Spain, vrivilla@cab.inta-csic.es

Propene is among the largest saturated or nearly saturated hydrocarbons that have been detected not only toward TMC-1 [1], but also in the warmer environment of the solar-type protostellar system IRAS 16293-2422 [2]. One of the next alkenes, isobutene, also known as 2-methylpropene, $(CH_3)_2C=CH_2$, is thus a promising candidate to be searched for in space. Its rotational spectrum was studied in the microwave region to some extent [3]. In this work, we have extended the measurement up to 370 GHz employing the Cologne (Sub-)Millimeter spectrometer. The molecule has two equivalent methyl rotors. The barrier height of the tops is high enough that the internal rotation splitting could either not be resolved or occur as symmetrical triplets. A few irregular quartets are also assigned, where splittings are up to ∼10 MHz. The analysis has been carried out with the ERHAM program [4] using the previous data as well. We have accessed transitions up to J = 60 and K_c = 41, greatly improving the spectroscopic parameters. With these, we have recently detected isobutene in the G+0.693 molecular cloud. The results of the Local Thermodynamic Equillibrium (LTE) fits for isobutene and its comparison with propene will also be presented.

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Speed-dependence line shape parameters of N_2- and O_2-broadened methane transitions in the ν_4 band– preliminary work

Vispoel B.[1], Lepère M.[1]

[1]*Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE) University of Namur (Unamur), Belgium: bastien.vispoel@unamur.be, muriel.lepere@unamur.be*

The study of line shape parameters provides valuable information on inter-molecular interactions as well as crucial data for radiative transfer modeling. For the latter, the accuracy of the spectroscopic parameters is directly related to the precision of the retrieved quantities[1]. Many works (see Ref.[2,3] and references therein) have shown that beyond-Voigt profiles, such as speed-dependent profiles, are more adequate to accurately reproduce experimental line shape profiles. Spectroscopic databases[4,5] report speed-dependent parameters for a limited number of molecules and transitions because of the experimental (and theoretical) challenges.

This work reports preliminary results on the study of speed-dependence line shape parameters for methane lines diluted in nitrogen and oxygen. The measurements were performed at room temperature using a high-resolution quantum cascade laser spectrometer which have an excellent signal-to-noise ratio. The experimental line shape profiles were fitted using a Voigt, a hard collision (Rautian – Sobel'man), and a speed-dependent Voigt model. The results are compared to available data in literature.

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Line shape measurement of a N_2-broadened nitrous oxide transition in the ν_1 band – preliminary work

Appart M.[1a], **Tran H.**[2], **Vispoel B.**[1], **Lepère M.**[1b]

[1]*Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, Belgium,* [a]*marine.appart@student.unamur.be,* [b]*muriel.lepere@unamur.be;* [2] *Laboratoire de Météorologie Dynamique, IPSL, CNRS, Ecole polytechnique, Université Paris-Saclay, Palaiseau, France*, *htran@lmd.ipsl.fr*

Nitrous oxide is the most important greenhouse gas after carbon dioxide and methane. It participates in the depletion of the ozone layer and its concentration is constantly increasing. For the analysis of atmospheric spectra, it is necessary to have accurate line parameters, in particular line shape parameters.

For a long time, Voigt profile fits on experimental line shape have been used to determine line parameters. The increasing improvement of the experimental devices, in particular thanks to lasers, has made it possible to highlight the fine effects occurring in the gas mixtures and influencing the line shape.

This work is devoted to the study of the P(16) line in the strong fundamental vibrational band ν_1 of the nitrous oxide diluted in nitrogen. Our measurements were carried out by high-resolution quantum cascade laser spectroscopy. The spectra were recorded at room temperature with a very low partial pressure of nitrous oxide (<0.5 mbar) while the nitrogen pressures were comprised between 10 to 200 mbar. Fits of theoretical models on experimental line shapes at each N_2-pressure were performed by using the Voigt profile, the hard collision model developed by Rautian-Sobel'man and a quadratic speed dependent Voigt profile. From these fits, we deduced the collisional half-widths at half maximum. By a linear regression of these values versus the nitrogen pressure, we obtained the collisional broadening coefficient for each line shape model. While several studies were dedicated to the measurement of this parameter in the ν_3 band of nitrous oxide, to our knowledge, in the ν_1 band, this transition was measured in Varanasi *et al.*[1] only, using the Voigt profile. We compared here our results with Ref. [1] but also with those obtained in the ν_3 band.

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Line shape parameter study of transitions in the ν_4 band of methane by mid-infrared dual-comb spectroscopy

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

[1]Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, Belgium, muriel.lepere@unamur.be; [2]IRsweep AG, Stäfa, Switzerland, jakob.hayden@irsweep.com, pitt.allmendinger@irsweep.com, andreas.hugi@irsweep.com, markus.mangold@irsweep.com

Even though methane is a minor component of Earth's atmosphere, it is the second most important greenhouse gas. Fundamental vibrational bands of this molecule are located in the mid-infrared region. Precise line shape parameter measurements are of crucial interest for the calculation of radiative transfer models which are necessary for a precise retrieval of methane concentrations[1].

Over the years, various high-resolution techniques were developed for molecular spectroscopy. One of the most recent ones is the quantum cascade laser based dual-comb spectrometer. This technology has already been proven well-suited for accurate line shape parameter measurements in the mid-infrared region[2]. This spectrometer allows to record high-resolution spectra (illustrated on Fig.1 which is a zoom of a small part of a measured spectrum) of more than 50 cm^{-1} in 20 minutes.

In this work, we studied N_2-broadened methane lines in the P-, Q- and R-branches of the ν_4 band. The measurements were performed at 293K (±1 K) with an optical path length of 15.0 cm. The partial pressure of methane was kept constant and very low (< 1 mbar), while the nitrogen pressure was comprised between 20 and 110 mbar. The collision-broadened line-widths were deduced from fits considering two different line-shape models: Voigt and Rautian-Sobel'man. We obtain a good agreement with the literature.

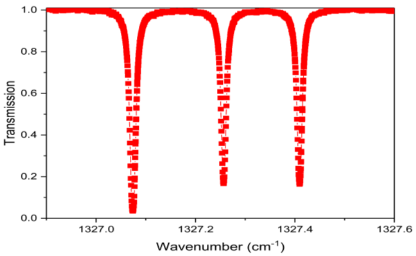

Fig. 1: Collision-broadened lines of methane diluted in nitrogen

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Discovery of interstellar C_5 molecule

Jacek Krełowski[1], **Rafał Hakalla**[1], **Wojciech Szajna**[1]

[1]*Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Poland,*
rhakalla@ur.edu.pl

The current work demonstrates the presence of the carbon chain C_5 molecule in translucent interstellar HI clouds. This species, the only five atom interstellar molecule, observable in dark, translucent clouds, seems to be observable in reasonably dense clouds, causing also rather high reddening. The poster shows two discovered spectral features of C_5: near 4975 and 5109 Å. The attempt to discover the 3789 Å C_4 feature gave the negative result.

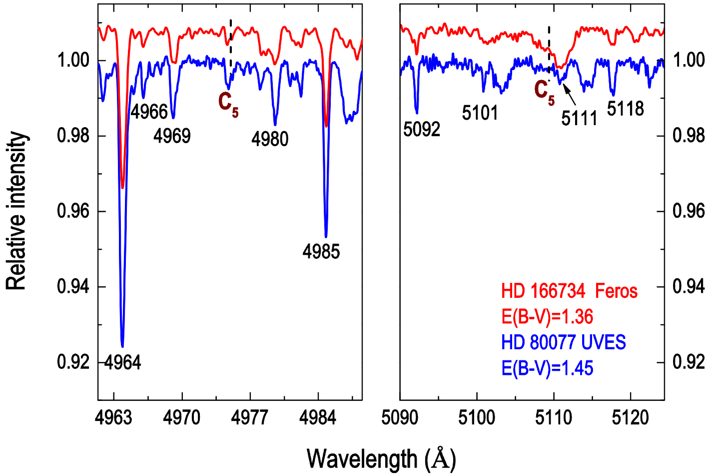

Fig. 1: The blown-up narrow ranges including the expected C_5 features. Note the presence of many DIBs [1,2] and differences in stellar spectra. The 5109/5111 DIB is very likely a composition of two profiles. The first one coincides with the expected 5109 C_5 feature.

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Fourier-transform spectroscopy of the $^{12}C^{18}O$ isotopologue and deperturbation analysis of the $A^1\Pi(v = 3)$ level

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

[1] *The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, 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.*
**m.malicka@prz.edu.pl*

This research was carried out using two complementary methods: *(i)* emission VIS-FT spectroscopy with the accuracy of about 0.005 cm^{-1} by means of the Bruker IFS 125HR spectrometer (University of Rzeszów) and *(ii)* absorption VUV-FT spectroscopy with the accuracy ca. 0.01 cm^{-1} using the wave-front-division spectrometer working as the end station on the DESIRS beamline (SOLEIL synchrotron). An effective Hamiltonian and *the term-value fitting method* were implemented. The precise deperturbation analysis of the $A^1\Pi(v = 3)$ level was performed by means of the PGOPHER program [1]. The data set was consisted of more than 400 spectral lines belonging to 5 bands: $B^1\Sigma^+ – A^1\Pi(0, 3)$, $C^1\Sigma^+ – A^1\Pi(0, 3)$, $A^1\Pi – X^1\Sigma^+(3, 0)$, $B^1\Sigma^+ – X^1\Sigma^+(0, 0)$ and $C^1\Sigma^+ – X^1\Sigma^+(0, 0)$. As the results, the improved deperturbed molecular constants of the $A^1\Pi(v = 3)$ level and their perturbers, spin-orbit and rotation-electronic (*L*-uncoupling) interaction parameters as well as their ro-vibronic terms were obtained. The current work is a continuation of the studies on the $A^1\Pi$ state in the CO isotopologues, made by our team [2-8].

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Insights into the non-covalent interactions of hydrogen sulfide with fenchol and fenchone from a gas-phase rotational study.

<u>Noureddin Osseiran</u>[1], Elias M. Neeman[1], Pascal Dréan[1], Manuel Goubet[1], Thérèse R. Huet[1]

[1] *Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France*

Monoterpenes ($C_{10}H_{16}$) and terpenoids (oxygenated terpenes) are biogenic volatile organic compounds (BVOCs) that are emitted naturally into the atmosphere mainly by vegetation. They contribute to Secondary Organic Aerosol (SOA) and tropospheric ozone formation,[1,2] mainly through oxidation pathways. Moreover, these molecules are capable of forming hydrogen-bonded complexes with surrounding atmospheric molecules, such as water.[3,4] The gas-phase non-covalent interactions in the endo-fenchol$\cdots$$H_2S$ and fenchone$\cdots$$H_2S$ complexes have been unveiled using rotational spectroscopy in a supersonic jet expansion, and quantum chemical calculations. In endo-fenchol, the hydrogen bond HSH$\cdots$OH together with dispersive interactions stabilize the system. In fenchone, the weak interaction HSH$\cdots$O=C allows an internal dynamic of H_2S.

The hydration of both endo-fenchol and fenchol molecules by water was previously studied, allowing detailed comparison.[5,6]

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Development of a high resolution chirped-pulse fourier transform millimeter wave spectrometer in combination with multipass optics

<u>Jonas Bosmann[1],</u> Pascal Stahl[1], Björn Waßmuth[1], Guido W. Fuchs[1], Thomas F. Giesen[1].

[1]*Universität Kassel, Germany, bosmannjonas@gmail.com*

We developed a high Power, high resolution Chirped Pulse Fourier Transfom millimeter wave (CPFTmmw) spectrometer in the range of 100-112.5 GHz allowing for resolution in the kHz range.[1] Measurements were conducted in combination with a multipass reflection optics (MRO) of 468 mm base length and an effective absolute absorption length of 33 m.[2] The reflection of the 100 GHz radiation from the mirror surfaces is high, but the diffraction-limited optics leads to losses that can only be compensated by a larger sizing of the optics. A new MRO optimized for 100 GHz with significantly reduced diffraction losses is being designed and built for future applications. The new setup is well suited to cover the entire W-band without the need to adjust the optics of the MRO. The spectrometer can be used in combination with molecular jets and pulsed molecular sources such as laser ablation. First results and comparison of multipass optics to the standard single pass configuration are presented.

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Cavity Ringdown Spectroscopy on jet-cooled astrophysically relevant molecules in the Mid-Infrared

Fabian Peterß[1], **Thies Neumann[1]**, **Matin Kaufmann[1]**, **Guido W. Fuchs[1]**

[1]*University of Kassel, Germany, f.peterss@physik.uni-kassel.de*

There is a surprising chemical diversity of molecules seen in space.[1]
Cold interstellar gas clouds in particular have displayed a high chemical diversity which is mainly due to complex organic hydrocarbon species.[2]
Although many species are known from radio astronomy, resolved infrared observations are sparse.[3] Astronomical observations in the infrared provide additional means to detect molecular species, since species with a weak dipole moment can instead be observed by their vibrational transitions.[4]

Our aim is to perform spectrally resolved and extremely sensitive measurements in the mid-infrared region utilizing the cavity ringdown (CRD) method on astrophysically relevant, jet-cooled organic molecules.
Our new experimental setup combines a „piezo scanned cavity" mid-infrared cw-OPO CRD spectrometer with a supersonic jet molecule source. The spectrometer achieves its highest sensitivity between 3.0 and 3.4 µm. In this region, O-H, N-H and C-H stretching vibrations can be probed.

Calibration measurements on the weak (1310)←(0000) combination band of jet-cooled N2O and first parts of a high resolution spectrum of jet-cooled propylene oxide in the C-H stretching vibration region will be presented.

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Terahertz spectroscopy of CaH in $v = 0$ and $v = 1$

Shota Suzuki[1], Tatsuki Sumi[1], Riku Fujiie[1], Fusakazu Matsushima[1],

Kaori Kobayashi[1], Yoshiki Moriwaki[1], Hiroyuki Ozeki[2]

[1] Department of Physics, University of Toyama, 3190 Gofuku, Toyama, 930-8555 Japan, kaori@sci.u-toyama.ac.jp;

[2] Department of Environmental Science, Toho University, Funabashi, Japan

Calcium monohydride CaH, a simple diatomic molecule, is an astronomical molecule that is identified using visible light transitions in the Sun and other stars. Numerous spectroscopic studies have been reported. We have also recently discovered a number of new vibrational levels in the $A^2\Pi$, $B/B^2\Sigma^+$, and $1^2\Delta$states in the visible ultraviolet using laser-induced fluorescence (LIF)[1-4]. In the microwave region, measurements of pure rotational spectra and analyses including hyperfine structures have been reported[5,6]. However, it was limited to the range of N = 2-1 and the highest frequency was about 500 GHz. In this paper, a new measurement of pure rotational transitions in the terahertz region is reported.

The terahertz spectra were measured with the tunable far-infrared spectrometer at the University of Toyama. CaH was produced by heating Ca to 750°C in a quartz cell to produce Ca vapor, which was then dc discharged under an atmosphere of H_2 and He (or Ar) gas.

The highest frequency of the ground state was about 3.7 THz and the highest frequency of the vibrationally excited state was about 1.9 THz. No hyperfine structure was resolved in our spectra. We plan to present analysis of these states. We will report the analysis of the pure rotational transitions and the results of a global fit combined with the frequencies of the previous infrared spectra[7].

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The Rotation-Tunneling Spectrum of Dimethylamine, $(CH_3)_2NH$

Holger S. P. Müller[1], Frank Lewen[1], Stephan Schlemmer[1]

[1]*Universität zu Köln, Germany, hspm@ph1.uni-koeln.de*

Methylamine (CH_3NH_2) was among the molecules detected early by means of radio astronomy. Detected initially only toward the giant star-forming region Sagittarius B2 close to the Galactic center. Recently, vinylamine ($C_2H_3NH_2$) and ethylamine ($C_2H_5NH_2$) were detected securely and tentative, respectively, toward the cold Galactic center source G+0.693−0.03 [1], making $(CH_3)_2NH$ a prime target for searches in space.

The microwave spectrum of dimethylamine was studied more than 50 years ago up to 45 GHz and $J = 8$. The spectrum displays an inversion splitting of the amino H atom of 1323 MHz, and the ^{14}N hyperfine splitting was well resolved for transitions with $J \leq 1$. The internal rotation splitting of the two equivalent methyl rotors was not resolved [2]. Very recently, a Fourier transform microwave spectroscopic (FTMW) study (2 − 40 GHz) of secondary aminesc revealed a small internal rotation splitting of order of ~200 kHz in dimethylamine [3].

We have studied the rotation-inversion spectrum of dimethylamine between 76 and 1091 GHz covering quantum numbers up to $J = 60$ and $K_a = 21$. Hyperfine splitting was resolved at least partly for many transitions and was treated in the analysis. The small internal rotation splitting was resolved in particular for transitions at lower frequencies or with lower quantum numbers, but was not considered thus far. The analysis was carried out with Pickett's spfit program. As the program is capable of treating high barrier internal rotation, we want to combine our data with the complete set of FTMW data. Attempts thus far suggest that the process is not straightforward, and it is not known to which extent it will work out.

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Microwave spectrum of CD_3OD in the $v_t = 0, 1, 2$ torsional states and a search of CD_3OD toward IRAS 16293−2422.

V. Ilyushin[1,2], R. Porohovoi[1], E. Alekseev[1,2], O. Dorovskaya[1], H. S. P. Müller[3], F. Lewen[3], S. Schlemmer[3], C. Maul[4], R.M. Lees[5], J. K. Jørgensen[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] Department of Physics, University of New Brunswick, Saint John, NB E2L 4L5, Canada; [6] Niels Bohr Institute, University of Copenhagen, Øster Voldgade 5−7, 1350 Copenhagen K, Denmark

We present[a] the results of our new study of the torsion-rotation spectrum of the fully deuterated isotopologue of methanol CD_3OD. The new microwave measurements were carried out from the millimeter wave range (starting at 34.5 GHz) to the THz range (up to 1.1 THz) using spectrometers in Kharkiv and Köln. The analysis is done using the rho axis method and the RAM36 program code. As it was the case[1] for CD_3OH our preliminary fits for CD_3OD show that the $v_t = 2$ torsional state is affected by perturbations propagating down through intertorsional interactions from non-torsional vibrational modes. Taking into account the astrophysical significance of methanol and its isotopologs we decided at the current stage of spectrum analysis to concentrate our fitting attempts at the ground and first excited torsional states of CD_3OD. With this limitation a fit within experimental error has been achieved (weighted rms ~ 0.78). In the poster the details of this new study will be discussed. By the time of the conference we also hope to present the first results of our search of interstellar CD_3OD toward IRAS 16293−2422 (PILS survey).

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The third torsional state of acetamide.

V. Ilyushin[1,2], R. Porohovoi[1], E. Alekseev[1,2], M. Pogrebnyak[1], H. S. P. Müller[3], F. Lewen[3], S. Schlemmer[3].

[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

We present[a] the results of our new study of the torsion-rotation spectrum of the acetamide molecule CH_3CONH_2. Despite the fact that acetamide was found to be ubiquitously present in the interstellar medium[1-3] its rotation spectrum was studied only up to $J_{\max} = 20$ so far[4]. The aim of the present study was to extend the quantum number range in the fit (thus improving the quality of predictions for higher excited rotational states) as well as the frequency range coverage. The new microwave measurements were carried out from the millimeter wave range (starting at 34.5 GHz) to the sub-millimeter wave range (up to 650 GHz) using spectrometers in Kharkiv and Köln. Our preliminary fits of $v_t = 0, 1, 2$ torsional states of acetamide with $J_{\max} = 62$ revealed some perturbations which we attribute to perturbations caused by the NH_2 wagging state at ~259 cm^{-1} (that propagate down to low-lying torsional states via intertorsional interactions). Extension of our assignments at the third excited torsional state of acetamide is a preparatory step toward explicitly accounting for this interaction with the NH_2 wagging state of acetamide. In the poster the details of this new study will be discussed.

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Non-Covalent Interactions of Triethylamine and its Complexes with Water Characterised by Rotational Spectroscopy

Isabel Peña[1,2], Shefali Saxena[1], Nanna Myllys[3], Yang Zheng[4], Qian Gou[4], M. Eugenia Sanz[1]

[1]*Department of Chemistry, King's College London, London SE1 1DB, UK, shefali.saxena@kcl.ac.uk, maria.sanz@kcl.ac.uk;*

[2]*Departamento de Química Física e Inorgánica, Universidad de Valladolid, Valladolid 47011, Spain, mipencal@uva.es;*

[3]*University of Jyväskylä, Jyväskylä, Finland, nanna.myllys@helsinki.fi;*

[4]*School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, China, qian.gou@cqu.edu.cn*

The non-covalent interactions of triethylamine (TEA) with water have been investigated using broadband and narrowband Fourier transform microwave spectrometers in the 2-18 GHz frequency range. Density functional and ab initio calculations have been performed to sample the potential energy surface of the complexes and support spectral searches. Two conformers of TEA have been identified in addition to the lowest-energy conformer previously reported[1]. For the complexes with water, two isomers of TEA-H_2O involving two different conformers of TEA and one isomer of TEA-$(H_2O)_2$ have been observed. All species have been unambiguously identified from the comparison between experimental and theoretical rotational and quadrupole coupling constants. In addition, several isotopologues of the two TEA-H_2O complexes have been observed, further confirming their assignment. In all complexes, one water molecule binds to the nitrogen atom of TEA through a N–H···O hydrogen bond and establishes secondary interactions with the hydrogen of TEA methyl groups. In TEA-$(H_2O)_2$ the second water molecule binds to the first and also interacts with TEA hydrogens through C–H···O hydrogen bonds. Understanding water interactions with amines is of relevance in atmospheric processes.

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Investigation of gas phase thermodynamics by the tool of high-resolution rotational spectroscopy

P. Buschmann[1], K. G. Lengsfeld[2], C. Höhne[2], D. Obenchain[2], D. McNaughton[3], J.-U. Grabow[2]

[1]Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Germany, philipp.buschmann@pci.uni-hannover.de; [2]Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Germany; [3]School of Chemistry, Monash University Clayton, Australia

Investigations by the variety of different spectroscopic methods reveal the possibility for a precise description of molecular properties. Since the obtained spectroscopic parameters characterize the energetic structure of the molecule with high accuracy also thermodynamic properties become accessible applying statistical thermodynamics. On the contrary high-resolution microwave spectroscopy has very rarely been used quantitatively to follow gas phase reactions and determine thermodynamic quantities macroscopically by relative intensity measurements (see e.g. [1]). A coherent comparison of both approaches (also with quantum chemical predictions) is presented. For this purpose a reinvestigation of before observed but incorrectly assigned succinc anhydride derivatives[2] has also been performed. Characteristics of the obtained high-resolution spectra including a rich fine and hyperfine structure, comparable to the perviously analyzed parent compound[3], are also discussed.

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Observation of vibrationally excited states of SiC_2 by Stimulated Emission Pumping (SEP) spectroscopy

Sederra D. Ross[1], Kin Long Kelvin Lee[2], Jonathan Flores[1], Michael C. McCarthy[2], Neil J. Reilly[1]

[1]Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125, United States, neil.reilly@umb.edu; [2]Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, United States

Recent observations of the evolved carbon star IRC+10216 with unprecedented high angular resolution have revealed a plethora of unassigned (U) rovibrational lines associated with the dust formation zone. Because SiC_2 is a known, abundant molecular constituent of this region, it is reasonable to posit that some fraction of the observed U lines arise from vibrationally excited levels of SiC_2 that are populated at elevated temperatures. At present, the laboratory rotational data that would permit testing of this hypothesis are largely absent: *ab initio* prediction of relevant spectroscopic constants has proved particularly challenging for SiC_2, and its excited vibrational levels are not efficiently populated in supersonic jet sources. However, the electronic transition responsible for the well-known blue-green Merrill-Sanford bands of SiC_2 admits Franck-Condon access to vibrational levels at least 4000 K above ground, inviting the application of SEP spectroscopy for the observation of vibrationally excited states. SiC_2 has been generated in our laboratory in a jet-cooled discharge of silane and acetylene, optically pumped via the M-S bands, and fluorescence depletion SEP spectra observed for dump transitions terminating in a variety of excited rovibrational levels for all three modes in the $\tilde{X}$-state. For known rotational levels of $1\nu_3$ and $2\nu_3$ (the pinwheel mode), the rotational energies derived from SEP spectra are in generally excellent agreement (a factor of at least 5 smaller than the dump laser linewidth) with previous observations, giving us good faith in our experimental procedure. The $1\nu_2$ level is notably perturbed, which accounts for its as-yet non-observation in the laboratory by rotational spectroscopy. A Fermi resonance with $6\nu_3$ depresses the $1\nu_2$ B and C constants significantly below the predictions of high-level theory. Vibrationally averaged rotational constants calculated using Fermi resonance mixing coefficients obtained from $\tilde{A}$-state zero-point dispersed fluorescence are broadly consistent with this interpretation.

Optical spectroscopy of ethynylbenzyl radical chromophores

Jonathan Flores[1], Sederra D. Ross[1], Sima Khani[1], Massimo Ruscitti[1], Daniel M. Hewett[1], Neil J. Reilly[1]

[1]*Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125, United States, neil.reilly@umb.edu*

The indenyl and phenylpropargyl radicals are the most stable isomers of C_9H_7 and have emerged as ubiquitous products in flames and hydrocarbon discharges. The *o*-, *m*-, and *p*-ethynylbenzyl isomers lie *ca.* 150-160 kJ/mol and 20-30 kJ/mol above the 1-indenyl and 1-phenylpropargyl minima, respectively, and can presumably form by barrierless addition of CH radical to phenylacetylene, but they are thoroughly unexamined spectroscopically. We have recently observed the $D_0 - D_1$ optical transitions of the *para* and *meta* variants by resonant two-color two-photon ionization and laser-induced fluorescence / dispersed fluorescence spectroscopy. For the *para* form, extension of the benzyl chromophore by a C_2 unit engenders a relatively (w.r.t. benzyl) strong transition that in large part submits to Franck-Condon analysis; while most of the vibronic structure in the much weaker transition of the *meta* isomer arises from intensity-borrowing among totally symmetric modes that are only weakly FC-active. Modes of a_1 symmetry of *para*-ethynylbenzyl are subject to pervasive Fermi resonances, as is established by single-vibronic-level emission spectroscopy. In the jet-cooled discharge, both *para* and *meta* forms are found in coexistence with 1-phenylpropargyl (which one might call α-ethynylbenzyl) at levels that cannot be explained by putative sample impurities unless computed oscillator strengths are too small by several orders of magnitude, suggesting rearrangement of all three radicals *via* an intermediate – perhaps ethynyltropyl – that remains undetected in the optical band. We have tentatively observed the *ortho* isomer near 528 nm; it is by far the least optically conspicuous of the ethynylbenzyl radicals in the discharge, presumably because it cyclizes to indenyl.

Fourier Transform spectroscopy of $^{13}C^{18}O$ and extended deperturbation analysis of the $A^1\Pi(v = 2)$ level

Stanisław Ryzner[1], Marzena I. Malicka[2], Alan N. Heays[3], Wim Ubachs[4], Robert W. Field[5], Nelson De Oliveira[6], Wojciech Szajna[1], Aleksandra Stasik[1], Andrzej Para[1], Izabela Piotrowska[1], Ryszard Kępa[1], Rafał Hakalla[1]

[1]*University of Rzeszów, Poland, sryzner@ur.edu.pl;* [2]*Rzeszów University of Technology, Poland;* [3]*J. Heyrovský Institute of Physical Chemistry, Czech Republic;* [4]*Vrije Universiteit, Netherlands;* [5]*Massachusetts Institute of Technology, USA;* [6] *Synchrotron SOLEIL, France*

The aim of this work was a thorough reinvestigate of the $A^1\Pi(v = 2)$ level in the $^{13}C^{18}O$ isotopologue. For this purpose, two complementary Fourier-transform techniques was used to obtain the spectra: (*i*) the emission spectroscopy in the visible region using Bruker IFS 125HR FT-spectrometer (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).

A deperturbation analysis of the $A^1\Pi(v = 2)$ 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, precise molecular parameters of the $^{13}C^{18}O$ investigated levels were obtained, including: molecular constants, interaction parameters as well as ro-vibronic terms of the $B^1\Sigma^+(v = 0)$, $B^1\Sigma^+(v = 1)$ and $C^1\Sigma^+(v = 0)$ levels.

The new results provide a significantly improved (compare to the previous one[1]) description of the complex set of intra-molecular interactions within the $^{13}C^{18}O$ $A^1\Pi(v = 2)$ level. 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[2,3,4,5,6.]

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FT-VIS emission spectroscopy of the $A^1\Pi$, ν = 0,1,2 levels of AlD: new data for the ExoMol line list database

Szajna W.[1], **Hakalla R.**[1], **Piotrowska I.**[1], **Ryzner S.**[1], **Stasik A.**[1], **Kolek P.**[1], **Para A.**[1], **Malicka M.I.**[2], **Kępa R.**[1], **Yurchenko S.N.**[3], **Tennyson J.**[3]

[1]*Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Pigonia 1 Street, 35-310 Rzeszów, Poland,* wszajna@ur.edu.pl
[2]*The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, Powstańców Warszawy 8 Street, 35-959 Rzeszów, Poland*
[3]*Department of Physics and Astronomy, University College London, London WC1E 6BT, UK,* s.yurchenko@ucl.ac.uk

High-resolution emission spectra of the AlD, $A^1\Pi - X^1\Sigma^+$ system have been observed with a Fourier transform spectrometer. The 0 − 0, 1, 2, 1 − 0, 1, 2, 3, 4 and 2 − 1, 2 bands were recorded with an instrumental resolution of 0.03 cm^{-1} and the best signal-to-noise ratio ca. 4000:1 for the 0 − 0 band. The 2 − 1 and 2 − 2 band were observed for the first time since 1934, when work of Holst and Hulthén[1] was published. The $A^1\Pi$, $\nu = 2$ vibronic level is a quasi-bound, predissociative state. Over, 400 ro-vibronic frequencies were measured with an absolute accuracy of about 0.0020 cm^{-1}. The present data were fitted using program PGOPHER[2] and molecular constants for the $X^1\Sigma^+$, $\nu = 0{-}4$ and $A^1\Pi$, ν = 0,1,2 levels[3] was obtained. Furthermore, the values of the rotational term of the $A^1\Pi$, ν = 0, 1, 2 levels were improved[4]. The current data were combined with the ground state results of White et al.[5] and the Dunham-like parameters (Y_{kl}) for the $A^1\Pi$ state of AlD were determined.

The new line positions of AlD reported here were used to improve the WYLLoT ExoMol line list for AlD[6]. The line list was computed using an empirical spectroscopic model based on literature data involving ν'=0 and ν'=1 ($A^1\Pi$) only and did not predict any bound or even quasi-bound states for AlD above ν'=1. Very recently, WYLLoT for AlH, built using a similar model, was used to identify AlH in the spectra of cool star Proxima Centauri (M6 V)[7]. This study showed the limitations of WYLLoT at high rotational excitations and for the $A^1\Pi$, ν=2 state. We present an improved spectroscopic model for AlD together with a new high-temperature line list for AlD covering $A^1\Pi$, ν = 0,1,2 computed using the Duo program suite[8].

This work illustrates the importance of experimental data for characterising complex potential energy curves, especially those with low dissociation limits or barriers, where extrapolations of the model can lead to inadequate or incorrect results.

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FT-UV emission spectroscopy of the B$^2\Sigma^+$- X$^2\Sigma^+$ (0-0,1,2,3 bands) system of $^{12}C^{17}O^+$

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

[1]Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszów, Pigonia 1 Street, 35-310 Rzeszów, Poland, wszajna@ur.edu.pl
[2]The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, Powstańców Warszawy 8 Street, 35-959 Rzeszów, Poland

The B$^2\Sigma^+$ ($\nu = 0$) level of $^{12}C^{17}O^+$ was investigated using the high-resolution, emission spectra obtained via Fourier transform spectroscopy of the (0 − 0), (0 − 1), (0 − 2) and (0 − 3) bands of the First Negative (B$^2\Sigma^+$ − X$^2\Sigma^+$) system. The (0−0) band was recorded for the first time[1,2,3]. The bands were recorded with an instrumental resolution of 0.05 cm^{-1} and the best signal-to-noise ratio ca. 100:1 for the 0 − 1 band. For obtaining spectra of the $^{12}C^{17}O^+$ isotopologue an air-cooled hollow-cathode lamp was used. The cathode was equipped with a cylinder made of graphite. Isotopically enriched molecular oxygen $^{17}O_2$ (Sigma-Aldrich, 98.1% of ^{17}O) was admitted to the lamp at about 0.2 Torr. The present data were elaborated with the PGOPHER program[4] and wide set of molecular constants for the X$^2\Sigma^+$, ν = 0−3[5] and B$^2\Sigma^+$, ν = 0 levels was obtained.

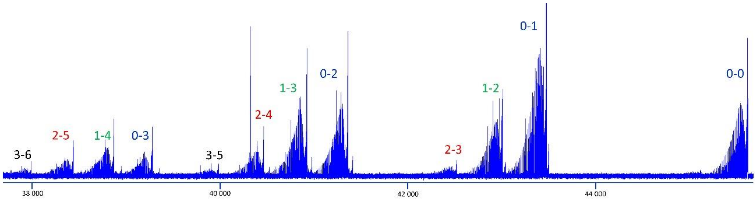

Fig. 1: An overview of the spectrum of the B$^2\Sigma^+$ − X$^2\Sigma^+$ system of $^{12}C^{17}O^+$ isotopologue in the 38 000 – 46 000 cm^{-1} region.

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A Rotational Spectroscopic and Theoretical Study of Tunneling in Substituted Benzoic Acid Heterodimers

Mohamad H. Al-Jabiri[1], **Mihael Eraković[2], Aran Insausti[3], Marko Cvitaš[4], Wolfgang Jäger[5]**

[1]University of Alberta, Canada, aljabiri@ualberta.ca; [2]Ruđer Bošković Institute,Croatia Mihael.Erakovic@irb.hr; Universidad del País Vasco (UPVEHU), Spain, Insausti@ualberta.ca; [4]Ruđer Bošković Institute, Croatia, mcvitas@phy.hr; [5]University of Alberta, Canada, wolfgang.jaeger@ualberta.ca

The complex tunnelling dynamics of double proton transfers in carboxylic acid dimers has been the focus of many theoretical and experimental studies.[1,2] Here we combine spectroscopic and computational approaches to model and understand how functional groups in substituted benzoic acid (BA) heterodimers can influence these dynamics. Dimers of BA with its 4-chloro-, 4-nitro-, and 4-amino-analogues were studied using a 2 to 6 GHz chirped-pulse Fourier transform microwave spectrometer, which is based on the design by Pates et al.,[3] to obtain experimental tunneling line splittings. Jacobi field instanton theory (JFI)[4,5] was used to compute tunneling splittings in the ground vibrational state. The use of the JFI method, which necessitates fewer number of potential energy and gradient calculations compared to other methods, enabled us to use ab initio on-the-fly potentials and compute the splitting in full dimensionality, in spite of the large system sizes. Furthermore, final expressions for the tunneling splittings provided a way to examine the influence of substituents on both the potential energy barrier height and shape, and on the vibrational modes, which can either promote or inhibit tunnelling.

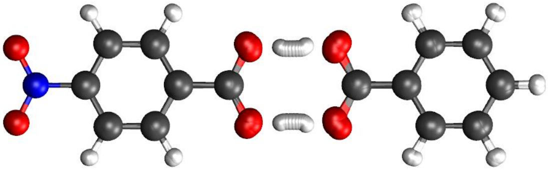

Fig. 1: Minimum action path for the double proton transfer in the benzoic acid – nitrobenzoic acid heterodimer.

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Home-built chirped-pulse spectrometers for complex molecules of astrophysical interest

B. Heyne[1], M. Hermanns[2], M. Fatima[2], S. Schlemmer[2]

[1]*University of Cologne, Germany, heyne@ph1.uni-koeln.de;* [2]*University of Cologne, Germany*

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. In addition, many of the organic molecules present or possibly present in space have their maximum transition intensity in this region at cold temperatures. 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 [1]. 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 4-cyanobiphenyl and its 13C isotopologs. 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 possibility to detect 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. Furthermore, we will compare the spectrometer with our emission spectrometer [2].

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Absorption cross sections of CHF_3 for atmospheric applications

Kirill Berezkin[1], Alexandra Domanskaya[1], Mi Eon Kim[1], Henning Bohlius[1], Jeremy J. Harrison[2], Gang Li[1] and Volker Ebert[1]

[1]*Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany,*
kirill.berezkin@ptb.de; [2]National Centre for Earth Observation, Space Park Leicester,
University of Leicester, Leicester, United Kingdom, LE1 7GH

The focus of the current work is on the trifluoromethane (CHF_3, a.k.a. HFC-23) which is a long-living atmospheric species with global warming potential (GWP) much higher (~12400) than that of carbon dioxide (=1) or methane (~30).

FTIR measurements of absorption cross sections of CHF_3 in pure gas and in mixtures with synthetic air at various pressures and temperatures were performed using Bruker-125 HR spectrometer at the PTB EUMETRICSPEC infrastructure[1,2]. Collecting quantitative spectral data for strong absorbent is bound to difficulties of careful controlling and determining low pressures, short path cells and adsorption-desorption effects. The current work profits from regular calibrations of the temperature and pressure sensors and from the usage of a state-of-the-art Sonimix 2106 gas mixer. Sonimix is based on sonic nozzle technology and allows to significantly improve the partial concentration stability and reproducibility.

The intensities of all major fundamental bands of CHF_3 in the NIR regions will be discussed and compared to the available literature data.

The measurements were performed in the frame of the EMPIR project "Metrology for Climate Relevant Volatiles Organic Compounds" (MetClimVOC)[3].

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GASMAS method for detection of gaseous pollutants in porous building materials

Michal Dostál[1,2], Jan Suchánek[1], Vanesa Richterová[2], Vít Klečka[2], Petr Bitala[2], Václav Nevrlý[2], Petr Konečný[3], Dita Vořechovská[4], Zdeněk Zelinger*[1]

*[1] J. Heyrovsky Institute of Physical Chemistry of the ASCR, v.v.i., Czech Republic, michal.dostal@jh-inst.cas.cz; [2]Faculty of Safety VSB – Technical University of Ostrava, Czech Republic; [3]Faculty of Civil Engineering VSB – Technical University of Ostrava, Czech Republic; [4]Faculty of Civil Engineering Brno University of Technology, Czech Republic, *corresponding author*

Gas absorption spectroscopy in scattering media (GASMAS)[1] is a relatively simple, robust and non-destructive method that can provide important information for the study of gas-solid interaction processes, i.e.: gas concentration, gas pressure or temperature and solid material properties (sorption/diffusion characteristics, porosity, etc.). The basic principle of the method is described in Fig. 1. where a diode laser beam is focused into a porous material where it is scattered (multi-reflected on the pore walls), the scattered radiation can then be detected by a sensitive detector.

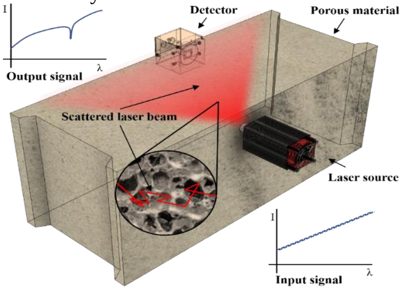

Fig. 1: Schematic representation of GASMAS technique

As a result of multi-reflection, the absorption path is multiplied and thus the detection of selected gaseous pollutants is more sensitive. The principles of wavelength modulation spectroscopy (WMS)[2] method is used for signal generation and processing. For example, the use of the GASMAS method may be of interest for studies of carbonation and chloride intrusion into concrete where current methods are time consuming, expensive and/or laborious.

Acknowledgement

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First observations of molecular lines with Irbene radio telescope

Eugene Alekseev[1,2,3,4], Vladislavs Bezrukovs[4], Artis Aberfelds[4],
Jānis Šteinbergs[4], Arturs Orbidans[4]

[1]*Institute of Radio Astronomy NASU, Ukraine, ealekseev@rian.kharkov.ua;*
[2]*V. N. Karazin Kharkiv National University, Kharkiv, Ukraine;*
[3]*Laboratoire de Physique de Lasers, Atomes et Molécules, Université de Lille, France;*
[4]*Engineering Research Institute "Ventspils International Radio Astronomy Centre" (VIRAC)*
Ventspils University of Applied Sciences, Latvia

The main radioastronomical instruments of VIRAC are 16 m and 32 m radio telescopes, respectively RT-16 and RT-32, with broadband cryogenic receivers covering frequency range of 4500 – 8800 MHz[1]. Both instruments previously were successfully applied for observations of maser radio sources[2,3]. We present the first observations of molecular lines. We choose formaldehyde line $1_{11} - 1_{10}$ which was firstly detected in 1969[4]. We observed this line in G173.70+2.89 and TMC-1 molecular cloud (see Fig.1). As previously[4] this line was detected in absorption against continuum sources.

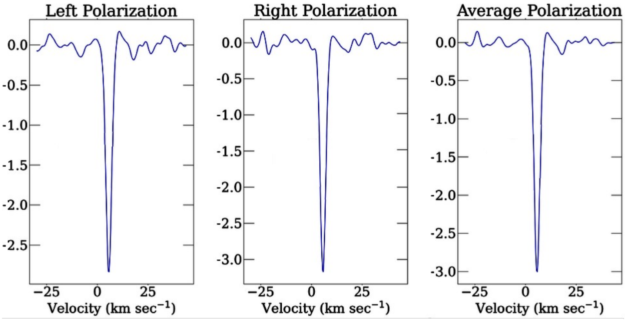

Fig. 1: The formaldehyde line 1_{11} - 1_{10} in the TMC-1 molecular cloud.

Signal-to-noise ratio of obtained records is very promising, so we hope to look for different molecular lines in the nearest future.

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Self- Broadening and Shifting Coefficients of Rovibrational Lines in the First Overtone Band of HBr

Alexandra Domanskaya[1], Ruslan E. Asfin[2], Christof Maul[3]

[1]*University of Göttingen, Germany, domav@yandex.com;*
[2]*St. Petersburg State University, Russia, R.Asfin@spbu.ru;*
[3]*Technische Universität Braunschweig, Germany, c.maul@tu-braunschweig.de*

The spectra of pure HBr in the region of the first of overtone were recorded at sub-atmospheric pressures with a Bruker IFS 120 HR with 0.003 cm^{-1} spectral resolution. Voigt profiles were found to describe adequately the isotopically resolved ro-vibrational lines. Self-broadening/shifting coefficients as well as the intensity of the lines were evaluated[1]. No statistically significant difference between broadening and shifting coefficients for different isotopologues was found.

The broadening coefficients are in good agreement with literature values, though having smaller uncertainties (~1% for $-10 \leq m \leq +8$ at the confidence level of 95%). A difference between the values in P-branch of our data and HITRAN is worth noting. HITRAN values were obtained by mirroring the broadening coefficients of the R-branch, therefore neglecting the broadening coefficients asymmetry which is definitively detected in our work. The shifting coefficients were reported for the first time to the best of our knowledge. Measured intensities are in reasonable agreement with previously reported values and with data of the HITRAN database.

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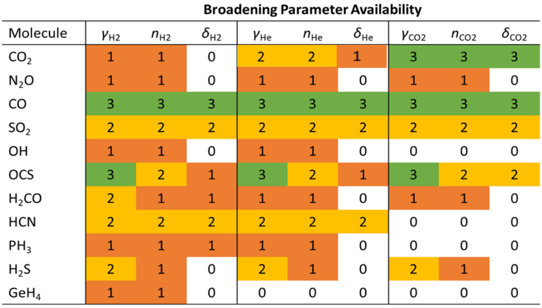
New Planetary-Relevant Broadening Data in HITRAN2020 and their Applicability to Generate Opacities under Planetary Conditions

Frances M. Skinner[1], Yan Tan[1,2], Shanelle Samuels[1], Robert J. Hargreaves[1], Robab Hashemi[1], and Iouli E. Gordon[1]

1. Center for Astrophysics | Harvard & Smithsonian, USA, igordon@cfa.harvard.edu ; 2 University of Science and Technology of China, Hefei, China,

The HITRAN2020 edition consists of a multitude of line-shape parameters associated with the pressure of "planetary" gases which are applicable to modeling and interpreting spectra of (exo)planetary atmospheres [1]. These new parameters comprise broadening due to the ambient pressure of H_2O [2], He, H_2, and CO_2 [3]. Planetary broadeners were initially added to the database during the HITRAN2016 edition for the line lists of SO_2, NH_3, HF, HCl, OCS, and C_2H_2 [4]. Henceforth, He, H_2, and CO_2 pressure broadening, temperature dependence, and in some cases, pressure-induced line shifts, have been added and/or updated for the line lists of CO_2, N_2O, CO, SO_2, OH, OCS, H_2CO, HCN, PH_3, H_2S, and GeH_4 [3]. Employing these planetary parameters in conjunction with the HITRAN Application Programming Interface (HAPI) [5], allows users to calculate a reliable planetary reference opacity. As a test case, we present our investigation [6] of how HITRAN broadening data can be used to model MW spectra under planetary conditions, with resultant opacities compared to available laboratory data. The lack of data for many systems of interest is highlighted in this Figure, and we would like to facilitate more measurements and calculations from the community/.



Broadening Parameter Availability

Molecule	γ_{H2}	n_{H2}	δ_{H2}	γ_{He}	n_{He}	δ_{He}	γ_{CO2}	n_{CO2}	δ_{CO2}
CO_2	1	1	0	2	2	1	3	3	3
N_2O	1	1	0	1	1	0	1	1	0
CO	3	3	3	3	3	3	3	3	3
SO_2	2	2	2	2	2	2	2	2	2
OH	1	1	0	1	1	0	0	0	0
OCS	3	2	1	3	2	1	3	2	2
H_2CO	2	1	1	1	1	0	1	1	0
HCN	2	2	2	2	2	2	0	0	0
PH_3	1	1	1	1	1	0	0	0	0
H_2S	2	1	0	2	1	0	2	1	0
GeH_4	1	1	0	0	0	0	0	0	0

Fig. 1: This figure highlights the lack of data availability for H_2, He and CO_2 broadening coefficients of different molecules. 0–no data available, 1–very few data available, 2–some measurements available, 3–relatively complete data set available.

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New line list for nine isotopologues of CO, based on semi-empirical PEF and DMF

Vladimir V. Meshkov[1], Aleksander Yu. Ermilov[1], Andrey V. Stolyarov[1], Emile S. Medvedev[2], Vladimir G. Ushakov[2], Iouli E. Gordon[3]

[1] Department of Chemistry, Lomonosov Moscow State University, Russia ; [2] Institute of Problems of Chemical Physics, RAS, Russia; [3] Center for Astrophysics | Harvard & Smithsonian, Atomic and Molecular Physics Division, USA, igordon@cfa.harvard.edu

The semi-empirical electric dipole-moment function (DMF) for the ground electronic state of the CO molecule has been constructed analytically in the entire range of the inter-nuclear distance by means of the simultaneous non-linear least-squares fitting (NLLSF) of the vetted experimental intensities for the principal isotopologue of CO and the ab initio dipole moment values[1]. The derived mass-invariant DMF possesses the physically correct asymptotic behaviour in both the united-atom and dissociation limits as well as reproduces the majority of the measured intensities in different bands within their experimental uncertainties. The resulting DMF and the mass-corrected potential-energy function[2] were used to calculate line lists for all (including radioactive) CO isotopologues in the wide range of vibrational and rotational quanta. The predicted intensities are compared with their experimental counterparts, including the most recent ones[3] that were not involved in the present NLLSF. We also show that discrepancies in calculated line lists and experimental measurements for minor isotopologues could primarily be attributed to uncontrolled abundances in the experimental cells and call for experiments that would involve mass-spectrometric measurements. The resultant line list[2] should be considered superior to previous efforts (including Li et al. work[4] that underlines current line lists for HITRAN and HITEMP) in terms of accuracy for both line positions and intensities.

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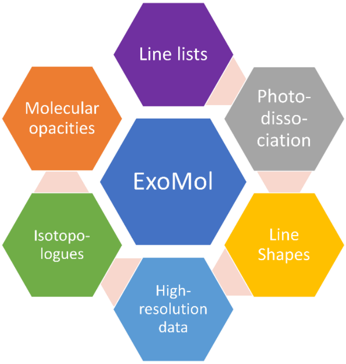
ExoMol 2022: Molecular data for studies of exoplanets and other hot atmospheres

Sergei N. Yurchenko, Jonatan Tennyson, Charles A. Bowesman, Ryan P. Brady, Elizabeth R Guest, Kyriaki Kefala, Anthony E. Lynas-Gray, Thomas Mellor, Alec Owens, Oleg L. Polyansky, Qianwei Qu, Mikhail Semenov, Andrei Sokolov, Wilfrid Somogyi, Andrei Sokolov, Apoorva Upadhyay, Samuel Wright, Jingxin Zhang

Department of Physics and Astronomy, University College London, London, United Kingdom, s.yurchenko@ucl.ac.uk



The discoveries of exoplanets have sparked significant activity on characterizing these planets through their spectra. These studies techniques have special requirements in terms of laboratory data needed to interpret observations: line positions, intensities and shapes, collision induced absorption, temperature and pressure dependent cross sections, molecular continuum data etc. [1]. We run the ExoMol project [2] which aims to provide molecular line lists, and increasingly other data (see the diagram), for studies of exoplanets and other astronomical atmospheres.

Our group ExoMol is one of the international leaders in providing molecular spectroscopic data for studies of exoplanets. ExoMol's techniques are based on the application of rigorous quantum mechanical methods informed by laboratory experiments, rather than on direct measurements. After ten years of the ExoMol project, 700 billion molecular transitions and two formal releases, ExoMol continues responding to the new challenges of the exoplanetary spectroscopy [3]. One of the key ExoMol activities is provision of high accuracy spectroscopic data for high resolution studies of exoplanetary atmospheres. Novel theoretical techniques are being used to provide similar high accuracy line lists for isotopically substituted species and to generate pressure broadening data. Finally, given the extreme conditions experienced by most observable exoplanets, namely high temperatures and huge levels of insolation, photodissociation is a major process chemical process. New methods are being developed to compute these cross sections and rates.

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ExoMol polyatomic line lists: Rovibrational line list for H_2CS and rovibronic line list for CaOH

Sergei N. Yurchenko[1], Thomas Mellor[1], Alec Owens[1], Jonathan Tennyson[1], Alexander O. Mitrushchenkov[2]

[1]Department of Physics and Astronomy, University College London, London, United Kingdom, s.yurchenko@ucl.ac.uk; [2]MSME, Université Gustave Eiffel, CNRS UMR 8208, Univ Paris Est Creteil, F-77474 Marne-la-Vallée, France

A computed line list for thioformaldehyde, H_2CS, applicable to temperatures up to T = 2000 K is presented. An exact kinetic energy operator, empirical potential energy surface (PES) and ab initio dipole moment surfaces are used as the input to the nuclear motion program TROVE [1]. The PES was refined by fitting to MARVEL energies of H_2CS generated as part of this project. The resulting line list, referred to as Thio, contains 52 million rotational-vibrational states and around 20 billion transition frequencies. Each transition includes associated Einstein-A coefficients and absolute transition intensities, for wavenumbers below 8000 cm^{-1} and rotational excitations up to $J = 120$. Room temperature spectra are compared with laboratory measurements.

Here, we also present the first comprehensive molecular line list of CaOH covering the $\tilde{A}\ ^2\Pi$ - $\tilde{X}\ ^2\Sigma^+$ rotation-vibration-electronic and $\tilde{X}\ ^2\Sigma^+$ - $\tilde{X}\ ^2\Sigma^+$ rotation-vibration bands computed using the computer program EVEREST [2]. The newly computed OYT6 line list contains over 24.2 billion transitions between 3.2 million energy levels with rotational excitation up to J=175.5. It is applicable to temperatures up to T=3000 K and covers the 0 – 35 000 cm^{-1} range (wavelengths $\lambda > 0.29$ μm) for rotational, rotation-vibration and the $\tilde{A}$ - $\tilde{X}$ electronic transition. The OYT6 line list has been generated using empirically-refined $\tilde{X}$ and $\tilde{A}$ state potential energy surfaces, high-level ab initio transition dipole moment surfaces and a rigorous treatment of both Renner-Teller and spin-orbit coupling effects, which are necessary for correctly modelling the CaOH spectrum.

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High resolution FTIR and diode laser spectroscopy of trifluoromethylacetylene and tetrafluoromethane in a supersonic jet expansion

V. Horká-Zelenková[1,2], M. Caviezel[2], G. Seyfang[2] and M. Quack[2]
[1]Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 182 21 Prague 8, Czech Republic, [2]Laboratorium für Physikalische Chemie, ETH Zürich, Vladimir Prelog Weg,2, Zürich CH-8093, Switzerland

We report high resolution infrared spectra in the CF stretching fundamental ranges of trifloromethylacetylene($CF_3{-}C\equiv C{-}H$, 3,3,3-trifluoropropyne) and of tetrafluoromethane (CF_4, R14, PCF-14, Halocarbon14). For the experiments, a diode laser setup combined with a supersonic jet expansion was applied, achieving approximate rotational temperatures between 5 and 10 K for CF_4, and slightly higher rotational temperatures (near 30 K) for CF_3CCH. At such temperatures, the rotational-vibrational structure of the spectra is greatly simplified for both molecules. The molecular beam spectra are complemented by high-resolution Fourier transform (FTIR) spectra at room temperature with nearly Doppler limited resolution (instrumental bandwidth 0.001 cm−1) using the Zürich prototype spectrometer ZP 2001 (Bruker IFS125). The analysis of the CF_3-symmetric stretching (A_1) fundamental ν_3 provides accurate spectroscopic parameters of the ground and excited vibrational states with a band centre $\tilde{\nu}_3 = (1253.4985 \pm 0.0015)$ cm^{-1} from a least squares adjustment to more than 1100 line data with a root mean square deviation d_{rms} less than 0.0003 cm^{-1}. The low-temperature spectra of the degenerate (F_2) ν_3 fundamental of CF_4 show a very simple structure of line clusters which can be analyzed with an approximate term formula. The spectra are essentially instrument limited with the smallest effective line width near 0.002 cm^{-1}. The results are discussed in relation to the data from the HITRAN tables, earlier FTIR data, and new frequency comb-based data for CF_4. We also discuss possible studies of nuclear spin symmetry conservation in CF_4, for which lower temperatures would be required, and a concept to study parity violation in CF_4 by a level crossing experiment using molecular beam spectroscopy. The complete results including a detailed discussion have been recently published [1].

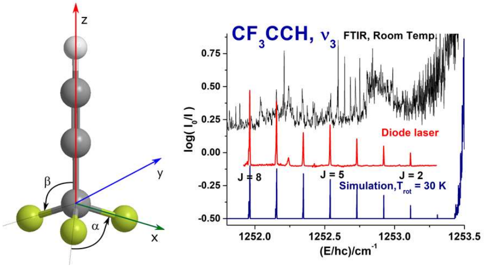

Fig. 1: CF_3CCH: Molecular structure and comparison of the room temperature spectrum with the spectrum obtained from the supersonic jet expansion.

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Millimeter wave spectra of vinylisocyanate and vinylketene, candidates for astronomical observations

Lucie Kolesniková[1], Jan Koucký[1], Karel Vávra[1], Kateřina Luková[1], Tereza Uhlíková[1], Patrik Kania[1], Jean-Claude Guillemin[2], Štěpán Urban[1]

[1]Department of Analytical Chemistry, University of Chemistry and Technology, Prague, Czech Republic, lucie.kolesnikova@vscht.cz; [2]Univ. Rennes, Ecole Nationale Supérieure de Chimie de Rennes, France

Interstellar detections of isocyanic acid[1], methylisocyanate[2,3], and very recently ethylisocyanate[4] open the question of the possible detection of the related molecule vinylisocyanate in the interstellar medium. Similarly, astronomical observations of ketene[5] places vinylketene among the species of potential interstellar relevance. In the present work, both vinyl species were generated by thermolysis of suitable precursors at 500 °C and their rotational spectra were recorded between 130 and 330 GHz using the Prague millimeter wave spectrometer[6]. The spectroscopic measurements and analyses presented here will allow searching for both molecules in the millimeter wave surveys of interstellar sources such as those recorded by Atacama Large Millimeter/submillimeter Array.

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Rotational spectrum of lactonitrile from microwave to millimeter wave region

Elena R. Alonso[1], Aran Insausti[2], Iker León[1], Lucie Kolesniková[3], José L. Alonso[1]

*[1]Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia,
Unidad Asociada CSIC, Universidad de Valladolid, Spain; [2]Departamento de
Química Física, Universidad del País Vasco (UPV-EHU), Spain; [3]Department of Analytical
Chemistry, University of Chemistry and Technology, Prague, Czech Republic,
lucie.kolesnikova@vscht.cz*

Complex organic molecules (COMs)[1] represent a sizable subset of interstellar species[2]. Among them, nitriles, the species bearing –C≡N functional group, have a strong prebiotic character as they represent plausible key players in the formation of amino acids, peptides, and nucleic acids. Here, we present a detailed rotational study of a potential candidate for astronomical search, lactonitrile ($CH_3CH(OH)CN$). The room-temperature rotational spectrum of this chiral nitrile has been measured and studied from 75 to 325 GHz. Additional measurements have been also made using a broadband CP-FTMW spectrometer in the 6–16 GHz region. Improved and extended sets of spectroscopic parameters with accuracy conducive to a reliable interstellar search are provided for two conformers of lactonitrile to the astronomical community.

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The shape of progesterone

Elena R. Alonso[1], Aran Insausti[2], Lucie Kolesniková[3], Iker León[1], José L. Alonso[1]

[1]Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Spain; [2]Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Spain; [3]Department of Analytical Chemistry, University of Chemistry and Technology, Prague, Czech Republic,
lucie.kolesnikova@vscht.cz

Solid samples of progesterone (m.p. 126 °C), one of the essential hormones, have been vaporized by laser ablation and probed in a supersonic expansion using a newly constructed chirped pulse Fourier transform microwave spectrometer working between 1.5 and 8 GHz. The analysis of around 150 rotational transitions revealed the existence of a single conformation. As for the related testosterone[1], progesterone adopts an extended configuration which is the most stable form predicted by quantum-chemical calculations. Due to the methyl group internal rotation, *A*–*E* splittings have been observed and allowed for the precise determination of the barrier height. The considerable molecular size of progesterone, one of the largest ever-attempted solid, illustrates the potential of the LA-CP-FTMW[2] technique in structural chemistry.

Acknowledgments: The authors thank the financial funding from Ministerio de Ciencia e Innovación (PID2019-111396GB-I00) and Junta de Castilla y León (VA077U16 and VA244P20).

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Millimetre-wave spectra and internal rotation of 2-iminopropanenitrile isomers

Kateřina Luková[1], Lucie Kolesniková[1], Jan Koucký[1], Karel Vávra[1], Patrik Kania[1], Jean-Claude Guillemin[2], Štěpán Urban[1]

[1]*Department of Analytical Chemistry, University of Chemistry and Technology, Prague, Czech Republic, e-mail: Katerina.Lukova@vscht.cz;* [2]*Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, France*

Millimetre-wave spectrum of 2-iminopropanenitrile (IPN) was measured using the Prague semiconductor absorption spectrometer[1] in selected frequency regions between 128 and 329 GHz. Due to the presence of the $–CH_3$ group, the molecule features a large amplitude motion, i.e. A-E splittings arise from the hindered methyl-top internal rotation. The newly measured rotational transitions of the most stable *Z*-isomer in its ground vibrational state were combined with the data from Groner et al.[2], and the A- and E-torsional species were analysed using the ERHAM and XIAM programs. The refined set of molecular constants including the three-fold barrier to internal rotation $V_3 = 572.59(14)$ cm^{-1} were obtained. Additionally, rotational transitions in the three lowest-lying excited vibrational states $\nu_{21} = 1$, $\nu_{14} = 1$, and $\nu_{20} = 1$of the *Z*-isomer were measured and assigned. Moreover, the rotational spectrum of the less stable *E*-isomer of IPN is reported for the first time. The joint analysis performed in the ERHAM and XIAM programs yielded the molecular parameters of this isomer and also the barrier to internal rotation of 508.05(22) cm^{-1}.

These new millimetre-wave data will support future astronomical searches for IPN in the interstellar medium.

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Laboratory rotational spectrum of 2-hydroxyprop-2-enal and its astronomical search with ALMA

Jan Koucký[1], Lucie Kolesniková[1], Kateřina Luková[1], Karel Vávra[1], Patrik Kania[1], Audrey Coutens[2], Jean-Christophe Loison[3], Jes K. Jørgensen[4], Arnaud Belloche[5], Štěpán Urban[1]

[1]Department of Analytical Chemistry, University of Chemistry and Technology, Prague, Czech Republic, jan.koucky@vscht.cz; [2] Institut de Recherche en Astrophysique et Planetologie (IRAP), Universite de Toulouse, UPS, CNRS, CNES, France; [3]Institut des Sciences Moleculaires (ISM), CNRS, Universite Bordeaux, France; [4]Niels Bohr Institute, University of Copenhagen, Denmark; [5]Max-Planck-Institut fur Radioastronomie, Germany

The $C_3H_4O_2$ family of isomers covers several species containing structural motifs typical for interstellar molecules, such as vinyl, hydroxyl, or aldehyde functional groups. Recent tentative detection of 3-hydroxypropenal and chemical modeling of its $C_3H_4O_2$ isomers suggest that another member of this family, 2-hydroxyprop-2-enal, could be abundant in IRAS16293-2422[1]. We performed laboratory measurements of millimetre-wave spectra of 2-hydroxyprop-2-enal with the Prague millimetre-wave semiconductor spectrometer[2] in two distinct frequency regions of 128–166 and 285–329 GHz. Hundreds of rotational transitions of 2-hydroxyprop-2-enal in the ground state and the lowest-lying excited vibrational state were assigned and analysed. Based on our data, the molecule was searched towards the solar-type protostar IRAS16293-2422 and the star-forming region Sagittarius B2(N). Results are provided in the present contribution.

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Terahertz measurements of rotational inversion transitions of ammonia isotopologues $^{14}NH_3$ and $^{15}NH_3$, including all deuterated forms

František Horák, Štěpán Urban

University of Chemistry and Technology, Prague, horakf@vscht.cz

Ammonia, the space thermometer, was the first polyatomic molecule to be measured in interstellar space, meaning that it has been well measured. However, due to the unavailability, until recently, of instrumentation with sufficient radiation intensity, many of its isotopologues transitions have yet to be measured in the terahertz region. Here, we use a high-resolution laser differential spectrometer to measure a significant part of this region (0.15–2.7 THz). This spectrometer uses two lasers: one always emits radiation with a fixed frequency; the other has a frequency that can be tuned according to temperature and current. To achieve a terahertz wave, a photomixer is used to subtract the frequencies of the two lasers from each other in real time; the wave passes through the sample into a second photomixer serving as a detector. By measuring all isotopologues in the 0.15–2.7 THz region in this way, over 500 new transitions were obtained. The SPFIT/SPCAT programs confirmed the correct assignment of the transitions before the transitions were then used to refine the values of the rotation and other constants related to the structures of the isotopologues. The resulting data provides a basis not only for making more accurate observations of interstellar space and its temperature but also for obtaining information about the phenomena that occur around proton stars and their extinction.

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Theoretical separation of inter and intra molecular vibrations in ambroxol hydrochloride

Tereza Uhlíková, Štěpán Urban

Departement of analytical chemistry, University of Chemistry and Technology, Technická 5, Praha 6, Czech Republic, tereza.uhlikova@vscht.cz

The crystalline structure and low-energy vibrations of ambroxol hydrochloride (A-HCl) were studied by solid state quantum chemistry calculations. The solid-state density functional theory (ss-DFT), with three different functionals (B3LYP, PBE and PW1PW) suggested the Cc crystallographic group for A-HCl and provide 40 vibrational normal modes up to 110 cm^{-1}.

The exact differentiation of whether some vibrational mode is unambiguously the intermolecular or the intramolecular mode is not fully possible since all the vibrational modes involve movements of all the nuclei of the interacting molecules. Nevertheless, the percentage contribution of the intermolecular motion to the particular vibrational mode is calculated. Furthermore, the nomenclature for complex vibrational modes is suggested.

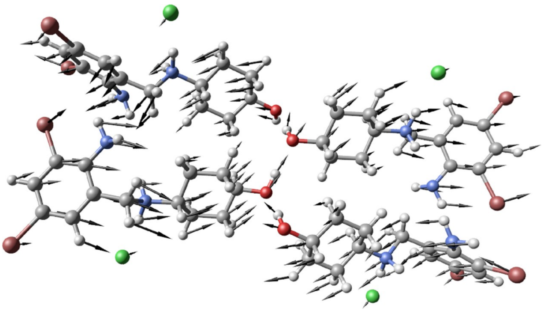

Fig. 1: Calculated normal mode of A-HCl within the ss-DFT/B3LYP at 45.55 cm^{-1} . This typical example of intermolecular vibration was denominated as the planar shuttle piston vibrational mode.

Acknowledgements

The Czech Science Foundation, project #18-08667S; and from the Czech specific university research (MSMT No. 20-SVV/2017). Computational resources were supplied by the “e-Infrastruktura CZ” (e-INFRA LM2018140) and ELIXIR-CZ project (LM2015047).

Session E

The Plíva Prize

August 31, Wednesday, 8:30 – 10:00

Quantum scattering calculations in diatom-diatom systems for accurate description of shapes of molecular resonances

H. Jóźwiak[1], M. Gancewski[1], A. Grabowski[2], A. Olejnik[1], K. Stankiewicz[1],
A. Zadrożny[1], P. Wcisło[1]

[1]*Institute of Physics, Faculty of Physics, Astronomy and Informatics,*
Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Toruń, Poland

[2]*Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland*

Studies of the shapes of molecular resonances provide information about molecular dynamics,[1] validate the potential energy surfaces,[2] and are crucial for a proper analysis of atmospheric spectra,[3] from which the concentration of an absorbing compound is retrieved. We present a theoretical description of the shape of molecular spectra, based on the state-of-the-art statistical model of the collision-perturbed optical coherence and quantum scattering calculations performed on *ab initio* potential energy surfaces. This approach has been validated on the H_2-He cavity enhanced spectra, for which a subpercent agreement between the calculated and measured spectral line profiles was obtained.[4] We discuss the ongoing efforts to employ this approach to more complex diatom-diatom systems, important for the analysis of gas giants' atmospheres (H_2-perturbed HD lines) and for the physics of terrestrial atmosphere (N_2-perturbed CO lines).[5] We present the new computational package developed in our group – **BIGOS** (**B**inary **I**nelastic scattering and **G**eneralized **O**ptical cross **S**ection package). The package allows the user to obtain the line-shape parameters from the potential energy surface for the scattering system by solving the close-coupling equations in the body-fixed frame of reference, and calculating the generalized optical cross sections.[6] Using BIGOS, we are able to include, for the first time, two subtle collisional effects in the theoretical analysis: the centrifugal distortion of the potential energy surface in a diatom-diatom system, and the effect of quantum indistinguishability on the shape of the molecular resonance.

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Title: High resolution molecular linelists for SrH and BaH

Shaun Donnelly[1], **Maire Gorman**[1], **Sergey Yurchenko**[2],**Jonathon Tennyson**[2]
[1]*Aberystwyth University, United Kingdom, shd7@aber.ac.uk;*
[2]*University College London, United Kingdom;*

Diatomic hydrides (BeH, MgH, CaH, SrH, BaH) have been of interest in the astronomical community since the early 1930s thanks to their tentative detection within sunspots. Early work by Richardson[1] and Babcock[2] inspired Wöhl[3] to investigate the existence of diatomic molecules, with the study covering 42 diatomic molecules including SrH and BaH. Thanks to recent experimental data by Shayesta et.al.[4] and Ram et.al.[5] it has been possible to generate linelists for SrH and BaH using the ExoMol methodology[6].

For both molecules *ab initio* calculations were undertaken in MOLPRO[7] 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[8] have been used with the Stuttgart effective core potentials[9] 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 C_{2v} framework for both SrH and BaH. This active space covers the four lowest dissociation limits for these molecules. Spin orbit calculations have been completed for these low lying states. The ground state R_e for SrH and BaH are calculated to be 2.1490 Å and 2.2312 Å; comparing favourably with experimental values of 2.1461 Å for SrH, and 2.2318 Å for BaH. Dissociations limits for the ground state's of SrH and BaH are calculated to be 14123.3313 cm^{-1} [10] and 16916.0667 cm^{-1} [11] agreeing with previous *ab initio* calculations conducted.

Linelists have been computed for the $E^2\Pi$ – $X^2\Sigma^+$ systems for SrH and BaH. Energy levels in these linelists have been fitted to an accuracy on the order of 0.01 cm-1 or better for the ground state and fitted to an accuracy on the order of 0.1 cm-1 or better for the Π states of each molecule. The maximum vibrational and rotational coverage of the SrH linelist are V_{max}=22, J_{max}=66.5, and for BaH are V_{max}=22, J_{max}=60.5. This coverage far exceeds the currently measured experimental transitions. The linelist covers 327540 transitions for the SrH system and 190569 transitions for the BaH system. The linelist will also include the major isotopologues of the molecules as well as their deuterium counterparts.

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Ab initio quantum scattering calculations for the CO–O_2 system and a new CO–O_2 potential energy surface: O_2 and air broadening of the R(0) line in CO.

Adam Zadrożny[1], Hubert Jóźwiak[1], Ernesto Quintas-Sánchez[2], Richard Dawes[2], Piotr Wcisło[1]

[1] *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Toruń, Poland, zadroznyadam@protonmail.com;*

[2] *Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409-0010, USA*

The CO molecule is an important trace gas used in the study of air quality[1] and for monitoring fossil fuel combustion.[2] It can also indirectly contribute to the climate change via its influence on ozone and methane concentrations.[3] Accurate knowledge of collision-perturbed line-shapes is crucial in the interpretation of remote sensing data.[4] Collisions of CO with O_2, the second most abundant constituent of the Earth's atmosphere, can significantly affect the shape of its spectral lines.

Here we present the first theoretical calculation of the O_2-induced pressure broadening of the R(0) spectral line in CO molecule. Our calculations are done in a fully quantum way by solving close-coupling quantum-scattering equations without any approximations. They were carried out using a new computational package, BIGOS, developed in our group. We also report a new highly accurate CO–O_2 potential energy surface on which we did the quantum-scattering calculations. The calculated collisional broadening agrees with the available experimental data in a wide temperature range. We combine this result with our previous calculations[5] for the same line in CO perturbed by N_2; the obtained air-perturbed broadening of the R(0) pure rotational line in CO and its temperature dependence perfectly agree with the HITRAN database. This result constitutes an important step towards developing a methodology for providing accurate *ab initio* reference data on spectroscopic collisional line-shape parameters for molecular systems relevant for Earth atmosphere and for populating spectroscopic line-by-line databases.

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Ab initio line-shape calculations for O_2-perturbed rotational lines in hydrogen halides

Artur Olejnik[1], Hubert Jóźwiak[1], Maciej Gancewski[1], Ernesto Quintas-Sánchez[2], Richard Dawes[2], Piotr Wcisło[1]

[1]*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Toruń, Poland; artur.olejnik@int.pl;*

[2]*Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409-0010, USA*

Accurate spectroscopic parameters for the hydrogen halides are important for the quantitative study of the Earth's atmosphere. Some hydrogen halides, namely HF and HCl, indirectly affect the ozone depletion process[1]. Monitoring their abundance in the stratosphere can help in characterization of ozone distribution. The HF and HCl gases occur in volcanic plumes[2]. Their measurement can provide information about the chemical composition of the volcanic gas mixture. O_2 molecule, which is the second most abundant constituent of the terrestrial atmosphere, plays a significant role in perturbing the shapes of the spectral lines of other molecules, including hydrogen halides[3].

Here we report the results of the first fully quantum scattering calculations for the electric dipole R(0) transition in hydrogen halides (HF and HCl) perturbed by O_2. For our quantum scattering calculations we use our new 4D potential energy surfaces for the HF-O_2 and HCl-O_2 systems. Close-coupling equations are solved using BIGOS - a new computational package developed in our group. Scattering S-matrices are used to calculate the generalized spectroscopic cross sections[4], which determine the collisional broadening and shift of the O_2-perturbed R(0) line in HF and HCl. We perform a detailed study of convergence of the obtained cross sections with respect to the size of the rotational basis set. Such investigations are important for populating spectroscopic databases.

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Anharmonic Vibrational Raman Optical Activity of Methyloxirane: Theory and Experiment Pushed to the Limits

Qin Yang,[1] Josef Kapitán,[2] Petr Bouř,[3] Julien Bloino[1]

[1] Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy, qin.yang@sns.it [2]Department of Optics, Palacký University Olomouc, 17. listopadu 12, 77146, Olomouc, Czech Republic, [3]Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo náměstí 2, 16610, Prague, Czech Republic

Combining Raman scattering and Raman optical activity (ROA) with computer simulations reveals fine structural and physicochemical properties of chiral molecules. Traditionally, the region of interest comprised fundamental transitions within 200-1800 cm-1. Only recently, non-fundamental bands could be observed as well. However, theoretical tools able to match the observed spectral features and thus assist their assignment are rather scarce. We will present an accurate and simple protocol based on a three-quanta anharmonic perturbative approach that is fully fit to interpret the observed signals of methyloxirane within 150-4500 cm-1. An unprecedented agreement even for the low-intensities combination and overtone transitions has been achieved, showing that anharmonic Raman and ROA spectroscopies can be valuable tools to understand vibrations of chiral molecules or to calibrate computational models.

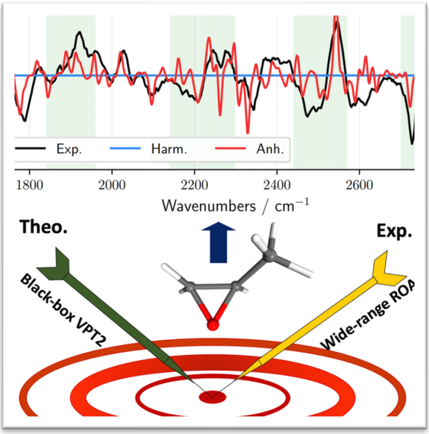

Fig. 1: High agreement between theory and experiment, even for overtones and combinations. The simulated spectra were gained from a black-box VPT2 scheme [1] up to three-quanta; the experiment spectra are measured with a customized wide-range ROA spectrometer[2]; methyloxirane in neat solution is used for the study.

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Strong Coriolis perturbation in isoquinoline spectra versus other PANHs': electronically dynamics pecularities on their structure

Sathapana CHAWANANON[1]*, Pierre ASSELIN[1]
[1]*Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, Paris, F-75005*
*France,*sathapana.chawananon@sorbonne-universite.fr*

The recent detection of cyano-naphthalenes within TMC-1 using radioastronomy [1] provided the first unambiguous confirmation of the interstellar PAH's hypothesis and raised new questions concerning the formation and destruction pathways of such systems in these cold environments. In the mid-infrared (IR) domain, the launch of the James Webb Space Telescope opens exciting perspectives to the exploitation of future astronomical observations. A tunable mid-IR quantum cascade laser (QCL) spectrometer coupled to a pulsed supersonic jet (SPIRALES set-up) has been recently implemented within the MONARIS laboratory that allows recording the rotationally resolved spectra of large heavy molecules at low rovibrational temperatures.[2]

In the continuity of our recent rovibrational jet-cooled studies on three centrosymmetric two-ring Polycyclic Aromatic Hydrocarbons (PAHs) [3], we extend our mid-IR investigations to N-substituted PAHs (or PANHs) including isoquinoline, quinoline, phthalazine, quinazoline and quinoxaline. Most of these spectra recorded in the in-plane ring CH bending and CC ring stretching regions have been successfully analyzed with the effective semi-rigid rotor Hamiltonian, except for the isoquinoline spectrum for which unexpected spacing Q branches are observed for every transition we recorded. Although isoquinoline is supposed to be a "nearly rigid body" due to the ring structure constraints, we failed to reproduce the structured Q branch observed using the semi-rigid rotor model. In a first step, Coriolis perturbation n-odd order terms have been introduced to resolve the fitting spectra problem. The new simulations rather well reproduced the Q-branch and the onset of P and R branches, indicating the model's correctness for the low J values. The Coriolis perturbation terms that we used to adjust spectra of isoquinoline could help to elucidate the "tunnelling" structure of this molecule. Coupled with its molecular constraints (ring structure), mechanical dynamics possibilities remain limited: thus, the "electronic dynamics" have been proposed to interpret the rovibrational spectra of this molecule, especially the possibility of stable mesomeric structures in aromatic compounds, where electronic delocalization can be viewed as the "superposition" of several Lewis structures.[4] Furthermore, the structural mesomeric dynamics in the vibrationally excited states turn to be challenging for theoretical proof and an experimental alternative would be to realize particular spectroscopic measurements of chemically analogous compounds to mimic the "electronically stimulated isoquinoline likelihood" and to obtain nearly similar spectra. A series of molecules with structural and electronic similarities compared to isoquinoline are currently investigated to demonstrate the evidence of this effect.

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Session F

The Plíva Prize

August 31, Wednesday, 10:30 – 12:00

Title: Millimeter and Sub-millimeter spectroscopy of doubly deuterated acetaldehyde (CHD_2CHO)

Judit Ferrer Asensio[1], Silvia Spezzano[1], Christian Endres[1], Valerio Lattanzi[1], Laurent H. Coudert[2], Paola Caselli[1]

[1]*Center for Astrochemical Studies, Max-Planck-Institut für Extraterrestrische Physik, Germany,* ferrer@mpe.mpg.de, spezzano@mpe.mpg.de, cendres@mpe.mpg.de, lattanzi@mpe.mpg.de, caselli@mpe.mpg.de *; [2]Institut des Sciences Moléculaires d'Orsay (ISMO), France,* laurent.coudert@universite-paris-saclay.fr

In the last years the number of multi-deuterated molecules detected in the Interstellar Medium (ISM) increased substantially. These molecules are found to be more abundant than expected when taking into account the ISM deuterium abundance ($D/H = 2.0 \pm 0.1 \times 10^{-5}$, Drozdovskaya et al.[1] and references therein). In order to better understand the nature of deuterium fractionation, and the interplay of the chemistry in the gas phase and on the surface of dust grains, chemical models need to be constrained by observations of singly- and multi-deuterated molecules. Doubly deuterated acetaldehyde (CHD_2CHO) has not been detected in the ISM yet as it has been studied in the laboratory only up to 40 GHz (Turner & Cox[2], Turner et al.[3]) and hence lacks an extensive spectroscopic study, in contrast with the singly-deuterated forms CH_2DCHO and CH_3CDO that were detected towards the protostellar core IRAS16293-2422B (Coudert et al.[4]). In order to allow the first detection of CHD_2CHO in the ISM, and understand its deuterium fractionation, we are studying its rotational spectrum in the millimeter and sub-millimeter frequency range. Its large amplitude torsional motion, giving rise to the tunneling splitting clearly visible in the figure, is accounted for using an approach similar to the one developed for the mono-deuterated species. The preliminary spectral catalogues thus built are used to search for this molecule in star-forming regions.

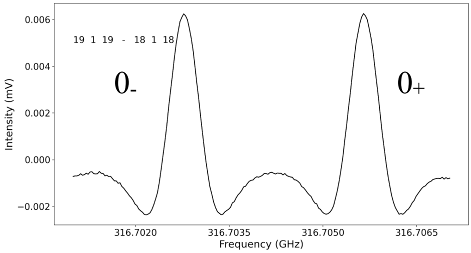

Fig: Tunneling splitting of the rotational transition J, Ka, Kc = 19, 1, 19 to 18, 1, 18.

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Systematic increase of the vibrational excitation of the water entity in the N_2−water van der Waals complex

Robin Glorieux[1], A. Bogomolov[2], M. Herman[3], N. Moazzen-Ahmadi[4], A. J. Barclay[4], B. Hays[1], T. Vanfleteren[3], C. Lauzin[1]

[1]*Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Chemin du cyclotron 2, 1348 Louvain-la-Neuve, Belgium, clement.lauzin@uclouvain.be;*

[2]*Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk, Russia;*

[3]*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.*

[4]*Department of Physics and Astronomy, University of Calgary, 2500 University Drive North West, Calgary, Alberta T2N 1N4, Canada, nmoazzen@ucalgary.ca;*

Rovibrational spectra of the N_2−water van der Waals complex were measured in the mid- and near-infrared ranges. Complexes were formed in a pulsed slit supersonic jet expansion and were probed using sensitive laser spectrometers. In this talk, I will present the rotationally resolved spectral signatures of the N_2−water van der Waals complex following different vibrational excitation of the water molecule in the complex. It is important to note that its dissociation energy is around $D_0 \sim 200$ cm−1 [1,2]. We started by probing the 1 OD stretch range of N_2−D_2O [3], i.e. the $(\nu'_1, \nu'_2, \nu'_3) \leftarrow (\nu''_1, \nu''_2, \nu''_3) =$ $(1, 0, 0) \leftarrow (0, 0, 0)$ and $(0, 0, 1) \leftarrow (0, 0, 0)$ vibrational bands, where ν_1, ν_2, ν_3 are the vibrational quantum numbers of the isolated water molecule. This range is around 12 times the dissociation energy of the complex. The spectra were assigned and the tunneling dynamics characterized in the frame of the G_8 molecular symmetry group. We then recorded and analyzed the first overtone of the OH stretch in the N_2−H_2O complex, i.e. the $(2, 0, 0) \leftarrow (0, 0, 0)$ and $(1, 0, 1) \leftarrow (0, 0, 0)$ vibrational bands. In this range, the excitation is nearly equal to 40 times D_0. These measurements are compared with the previous ones, notably the tunneling splittings. Finally, measurements were performed involving the excitation of all the modes of the water unit in N_2−D_2O, i.e. $(1, 1, 1) \leftarrow$ $(0, 0, 0)$. At the end of this talk, I will present perspectives to perform even larger vibrational excitation of the water unit in the N_2−water van der Waals complex and discuss the dissociation dynamics as a function of the probed vibrational state.

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Spectroscopic and Computational Characterization of 2-aza-1,3-butadiene, a Molecule of Astrochemical Significance

Ningjing Jiang,[1] Mattia Melosso,* [1, 2] Luca Bizzocchi,[1] Silvia Alessandrini,[3] Jean-Claude Guillemin,[4] Luca Dore,[1] and Cristina Puzzarini* [1]

[1]*Dipartimento di Chimica “Giacomo Ciamician”, Università di Bologna.*

[2]*Scuola Superiore Meridionale, Università di Napoli Federico II .*

[3]*Scuola Normale Superior.*

[4]*Univ Rennes, Ecole Nationale Sup erieure de Chimie de Renne*

Being N-substituted unsaturated species, azabutadienes are molecules of potential relevance in astrochemistry, ranging from the interstellar medium to Titan's atmosphere. 2-Azabutadiene and butadiene share a similar conjugated π system, thus allowing investigation of the effects of heteroatom substitution. More interestingly, 2-azabutadiene can be used to proxy the abundance of interstellar butadiene. To enable future astronomical searches, the rotational spectrum of 2-azabutadiene has been investigated up to 330 GHz. The experimental work has been supported and guided by accurate computational characterization of the molecular structure, energetics, and spectroscopic properties of the two possible forms, *trans* and *gauche*. The *trans* species, more stable by about 7 kJ/mol than *gauche*-2-azabutadiene, has been experimentally observed, and its rotational and centrifugal distortion constants have been obtained with remarkable accuracy, while theoretical estimates of the spectroscopic parameters are reported for *gauche*-2-azabutadiene.

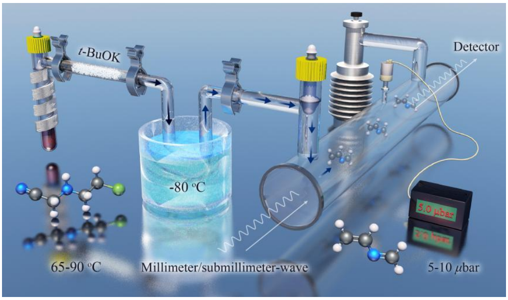

Fig. 1 The synthesis of 2-azabutadiene, and its rotational spectrum was recorded with a frequency-modulation spectrometer.

CO_2 collision-induced line parameters for the ν_3 band of CH_4 measured using a hard-collision speed-dependent line shape and the relaxation matrix formalism

Thibault Bertin,[1] **Jean Vander Auwera**[1]

[1]*SQUARES, Université Libre de Bruxelles, C.P. 160/09, 50 avenue F.D. Roosevelt,*
B-1050 Brussels, Belgium, thibault.bertin@ulb.be

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.[1-6]

High resolution Fourier transform spectra of methane diluted in carbon dioxide at total pressures up to 800 hPa have been recorded at room temperature in the pentad region around 3.3 µm. Their analysis is being carried out using multi-spectrum fitting techniques[7] and a hard-collision speed-dependent line mixing profile developped by Ciuryło and Pine.[8] Results will be presented and compared to previous work, including our initial measurements carried out using first order line mixing.

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Acknowledgement

T. Bertin thanks the FRIA (Belgium) for a PhD fellowship. This work is financially supported by the "Fonds de la Recherche Scientifique"–FNRS (Belgium).

Challenging the limits of rotational spectroscopy: gas phase structural elucidation of multiconformational macrolactones

Maider Parra-Santamaria[1,2], Imanol Usabiaga[1], Aran Insausti.[1,2], Elena R. Alonso[3], Francisco J. Basterretxea[1], Camilla Calabrese[4], Emilio J. Cocinero[1,2]

[1] Spectroscopy Group, University of the Basque Country, Spain, maider.parra@ehu.eus; [2]Biofisika Institute, Spain, emiliojose.cocinero@ehu.eus; [3] Grupo de Espectroscopía Molecular (GEM), Universidad de Valladolid, Spain, elenarita.alonso@uva.es; [4] Group of Spectroscopy of Plasmas and Supersonic Jets, Universidad de Valladolid, Spain, calabrese.cami@gmail.com

Exploring the conformational landscape of multiconformational systems can be quite complicated due to the competition among intramolecular forces. To address this issue, high-resolution gas-phase microwave spectroscopy is one of the most accurate techniques, able to isolate different conformers unequivocally [1] without masking effects. Macrolactones, cyclic structures with one or more ester linkages consisting of alkyl ring architecture of 12 or more atoms, are a good example of structural complexity because of the rich conformational panorama they present. In this study, we have performed the 3D structural analysis of two macrolactones of increasing size: oxacyclotridecan-2-one (*C12*) and 16-hexadecanolide (*C15*). Uncommonly, we observed 22 conformers for *C12* and 20 for *C15*, a record in conformational detection. This was possible thanks to the development of the chirp-pulsed (CP) technology, which has made affordable molecular targets previously out of reach in terms of size and conformational complexity. [2]

These two case studies push the limits of the CP technique and quantum chemistry calculations, due to their virtually strain-free cyclic structures. This rotational study fills the gap in the understanding of the relationship between shape and physicochemical properties of molecules.

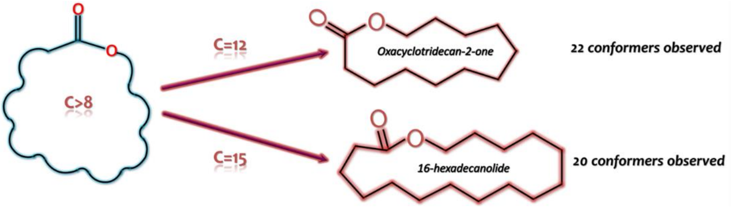

Fig. 1: Sketch of the studied macrolactones.

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First Observation of the HONO-H_2O Complex with Microwave Spectroscopy

Kenneth J. Koziol[1], Ha Vinh Lam Nguyen[2], Tarek Trabelsi[3], Safa Khemissi[2], Martin Schwell[2], Joseph S. Francisco[3], Isabelle Kleiner[2]

[1]Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany, koziol@pc.rwth-aachen.de; [2]Laboratoire Interuniversitaire des Systèmes Atmosphèriques (LISA), CNRS UMR 7853, Université Paris-Est Créteil, Université de Paris, 61 avenue du Général de Gaulle, F-94010 Créteil, France; [3]Department of Earth and Atmospheric Science and Department of Chemistry, University of Pennsylvania, 251 Hayden Hall, Philadelphia, PA 19104, USA

The impact of gaseous nitrous acid (HONO) in atmospheric chemistry is well described, being a major source of OH radicals acting as a strong oxidant.[1] In standard conditions, HONO is in equilibrium with various nitrous oxides under rapid decomposition at daytime. However, results by Lammel and Cape describe a steady production of OH radicals by HONO in the atmosphere whose source by the complex of HONO with water.[2] Recent experiments have revealed that HONO remains stable in an aqueous environment as the HONO · H_2O complex, supporting studies of its greater stability in environments with higher humidity.[3]

In the present work, gaseous HONO · H_2O was generated in a laboratory scale and investigated with two molecular jet Fourier transform microwave spectrometers operating from 2 to 40 GHz. To guide the experimental observation, geometry optimizations were performed to obtain rotational constants using the standard coupled-cluster theory with single and double excitations. The HONO · H_2O spectrum has been assigned with the ^{14}N quadrupole coupling taken into account. Further splittings by the ortho-hydrogens, resulting from spin-spin coupling interactions could be observed. Comparing the results to those of the dimethylamine-water complex[4], confirmed an absence of the water tunnelling motion.

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Session G

The Plíva Prize

August 31, Wednesday, 14:15 – 15:45

High-resolution rotational spectroscopy of APN, a promising amino-acid precursor.

Davide Alberton[1], Lattanzi Valerio[2], Christian Endres[2], Paola Caselli[2]

[1]MPE, Germany, alberton@mpe.mpg.de; [2]MPE, Germany

The detection of the simplest amino acid, glycine, by in situ measurements on comet 67P/C-G has sparked the growing interest of astrochemists in complex organic molecules (COMs)[1]. The formation pathways, precursors, and intermediates of amino acids in the interstellar medium (ISM) are under debate, and numerous are efforts to detect this class of molecules directly in space. Drozdovskaya et al. (2019)[2], outlined a CHO-, N- and S-bearing volatiles correlation between comet 67P/C-G and IRAS 16293-2422, a low-mass binary protostellar system thought to be analogous to the youngest stages of formation of our Solar System. This might suggest the preservation of prestellar and protostellar volatiles into cometary bodies, possibly indicating the formation of glycine at these same early stages of star formation[3]. Likewise, other amino-acids can form in these initial stages as well. The two best-known pathways leading to these building blocks of life are photochemical and through the Strecker synthesis, and both involve the hydrogenation of an aminonitrile molecule in their final step[4]. Aminoacrylonitrile (3-amino-2-propenenitrile, APN), which can be readily prepared in the gas phase from cyanoacetylene (HCCCN), ubiquitous in the ISM, and ammonia (NH_3), is, therefore, a prime candidate for such a search[4]. We used the CAS Laboratories' high-resolution absorption spectrometer (CASAC) to record and characterize the rotational spectrum of this aminonitrile in the gas phase mm-wavelength up to the THz range. The comprehensive measurements enabled the determination of accurate rotational and distortion constants, which were used to compile a catalog with accurate transition frequencies for the search for APN in space.

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Measurement of perfluoro-n-octane absorption cross-sections between 515 and 1500cm^{-1} from 305 to 350K

Muhammad Osama Ishtiak[1], Orfeo Colebatch[1], Karine Le Bris[2], Paul J. Godin[3], Kimberly Strong[1]

[1]*Department of Physics, University of Toronto, Canada, osama.ishtiak@mail.utoronto.ca*

[2]*Department of Physics, Saint Francis Xavier University, Canada*

[3]*Institute for Quantum Computing, University of Waterloo, Canada*

Perfluorocarbons (PFCs) are fully fluorinated greenhouse gases. These compounds are chemically inert due to their C-F bonds and therefore have atmospheric lifetimes of thousands of years. Although regulated under the Kyoto Protocol, atmospheric concentrations of PFCs with four or more carbon atoms have increased.[1] However, perfluoro-n-octane emissions remained constant up to 2012.[2] Spectral data are required to calculate metrics like radiative efficiency and global warming potential to quantify the climate impact of perfluoro-n-octane. A recent review paper provided only two experimental sources of spectral data, one at 296K and the other at 297K.[2,4] Here we provide a set of absorption cross-sections in the range 515-1500cm^{-1} at 0.1cm^{-1} resolution for five temperatures between 305K and 350K. The cross-sections agree with the data sets.[2,4] The preliminary radiative efficiency and global warming potential values for 305K, obtained via the updated Pinnock method[3], are within 10% of previously calculated literature values. Furthermore, the measured values do not change significantly as the spectral temperature rises from 305K to 350K. Therefore, our results validate previously collected experimental data and increase the range of temperatures available for measured perfluoro-n-octane cross-sections.

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The water vapor self- and foreign-continuum at room temperature in the 1.25 µm window

Aleksandra O. Koroleva[1], Samir Kassi[1], Didier Mondelain[1], Alain Campargue[1]

[1]LIPhy, Université de Grenoble Alpes, France, aleksandra.koroleva@univ-grenoble-alpes.fr

The water vapor self- and foreign-continuum are newly measured at room temperature in the high energy edge of the 1.25 µm window by using highly stable and sensitive cavity ring-down spectroscopy (CRDS, [1]).
Self-continuum cross-sections, C_S, are derived between 8290 and 8620 cm^{-1} at 29 selected spectral points by using pressure ramps (up to 15 Torr) of pure water vapor. Purely quadratic pressure dependence is obtained for the absorption coefficient at each measurement point. Although the spectral measurement points were chosen to minimize the contribution of resonance line absorption, the latter represents between 30 and 70 % of the measured absorption in the studied region. The self-continuum measurements are found consistent with a previous study of the low-frequency edge of the 1.25 µm window [2]. The frequency dependence of the retrieved C_S values shows an overall good agreement with the MT_CKD values. Nevertheless, an additional broad absorption feature is observed with a centre near 8455 cm^{-1}. It is tentatively interpreted as a possible impact of the uncertainties on the resonance line contribution on the derived C_S values or as possible evidence of a band of the bound dimers, $(H_2O)_2$.
Foreign-continuum cross-sections, C_f, are derived for humidified nitrogen, humidified oxygen and humidified air between 8120 and 8500 cm^{-1} by using pressure ramps (up to 750 Torr with 10000 ppm of H_2O) at 5 selected spectral points for each gas mixture. Although data treatment is in progress, the H_2O-air and H_2O-N_2 C_f cross-section values seem to be comparable while the H_2O-O_2 C_f value appears to be significantly smaller. A satisfactory agreement of the retrieved C_f for H2O-air mixture with the MT_CKD model is demonstrated. To the best of our knowledge, it is the first H_2O-air, H_2O-N_2, H_2O-O_2 foreign-continuum study in this frequency range.

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Approaching the free rotor limit: Extremely low methyl torsional barrier observed in the microwave spectrum of 2,4-dimethylfluorobenzene

Safa Khemissi[1], Martin Schwell[1], Isabelle Kleiner[2], Ha Vinh Lam Nguyen[1,3]

[1]*Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France,*
Safa.Khemissi@lisa.ipsl.fr; Martin.Schwell@lisa.ipsl.fr; Lam.Nguyen@lisa.ipsl.fr;
[2]*Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France,*
Isabelle.Kleiner@lisa.ipsl.fr;
[3]*Institut Universitaire de France (IUF), F-75231 Paris, France*

Dimethylfluorobenzene isomers (DMFB) are aromatic heterocyclic volatile organic compounds (VOCs). These VOCs are methylated toluene derivatives, one of the most prevalent aromatic hydrocarbons in the troposphere and considered as atmospheric pollutants[1]. The DMFB isomers are of astrophysical interest as precursors of polycyclic aromatic hydrocarbon (PAH) formation. Therefore, there is a fundamental interest in monitoring these molecules in the gas phase. Three isomers of DMFB have already been studied[2-4]. The fourth isomer 2,4-dimethylfluorobenzene (24DMFB) will be presented here. The spectrum of 24DMFB has been recorded between 2.0 and 26.5 GHz using a molecular jet Fourier transform microwave spectrometer[5]. To guide the spectral modelling and analysis, quantum chemical calculations have been carried out. Due to the internal rotation of two inequivalent methyl groups, all rotational transitions split into quintets. The spectral analysis was challenging due to the fact that one of the two methyl groups in 24DMFB have a torsional barrier of about 1 cm^{-1}, leading to large splittings between the torsional species. Using the *SFLAMS*[6] program, the assignments were checked by fitting separately each of the five torsional species. A global fit of 813 torsional lines was performed using the program *XIAM*[7] and *ntop*[8], giving standard deviations of 578.4 kHz and 13.3 kHz, respectively. The torsional barriers of the methyl groups in the *ortho* and *para* positions were determined to be 226.2087(16) cm^{-1} and 1.4387(58) cm^{-1}, respectively.

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Rotational spectroscopic study of cysteamine and its monohydrate complex

Wentao Song[1], Assimo Maris[1], Charlotte Cummings[2], Luca Evangelisti[1],
Nick Walker[2*], Sonia Melandri[1*]

[1]*University of Bologna, Italy, sonia.melandri@unibo.it;*
[2]*Newcastle University, United Kingdom, nick.walker@newcastle.ac.uk;*

Cysteamine ($NH_2CH_2CH_2SH$), a molecule of potential astrobiological interest, has not yet been detected in the interstellar medium. We have studied its rotational spectroscopy and found five conformers (gGt, gGg, g'Gg, g'Gg' and g'Gt). The search it in the molecular cloud G+0.693–0.027 was not successful but an upper limit to its abundance has been determined and the molecule. is still promising for other observations. [1]

Also for an interstellar related molecule, it is always interesting to investigate its water complex in order to comprehend its behaviour on dust grains covered by a mantle of water ice. For this purpose, we studied the rotational spectroscopy of cysteamine monohydrate. To explore its conformational space, we utilized the Conformer–Rotamer Ensemble Sampling Tool software (CREST) [2]. The obtained conformers were optimized at the B3LYP-D3(BJ)/def2-TZVP level of calculation. Frequency calculations were then run on the five more stable species (relative energy below 600 cm^{-1}) to confirm that they were real minima. Among them, the global minimum consists of the cysteamine monomer with configuration g'Gg combined with a water molecule inserted between the sulphydryl and amino groups, forming a SH-OH-N non covalent "bridge".

A spectral survey (6.5-18.5 GHz) performed with both Pulsed Jet (UNIBO) and Chirped-pulse (NCL) Fourier transform microwave spectrometers confirmed this landscape, allowing to observe and assign the global minimum species. Subsequently, we studied the ^{34}S and ^{18}O mono-substituted isotopologues. All the observed species showed a hyperfine structure due to the ^{14}N quadrupole coupling interaction. However, the hyperfine structures for these three species show very different patterns, which will be discussed.

Despite the fact that the g'Gg conformer is not the global minimum (gGt) of the cysteamine moiety, the possibility to form both intra-molecular and multiple inter-molecular bonds makes it the best candidate for water complexation.

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Broadband rotational spectroscopy of 2,4,6-cycloheptatriene-1-carbonitrile: a potential interstellar molecule

GAYATRI BATRA[1], LAURA PILLE[1], BENJAMIN E. ARENAS[1], DONATELLA LORU[1], MELANIE SCHNELL[1]

[1] *Deutsches Elektronen-Synchrotron DESY, Germany, gayatri.batra@gmail.com*

The recent astronomical observations of the simplest aromatic nitrile, benzonitrile, *c*-C_6H_5CN, followed by a five-membered [1,2] and a bicyclic [3] CN-functionalized ring in TMC-1 have opened up an entirely new field of complex organic molecules (COMs) in space. These new findings provided an impetus to the laboratory rotational spectroscopy studies of larger CN-functionalized rings. One such example is 2,4,6-cycloheptatriene-1-carbonitrile (2,4,6-CHT-1-CN), a seven-membered ring with a CN group attached to the sp^3-hybridized carbon atom. With a permanent electric dipole moment of 4.3 D and decent vapor pressure, the molecule is an excellent candidate for laboratory rotational spectroscopy.

Experiments were performed using chirped-pulse Fourier transform microwave and millimeter wave spectroscopy in the 18-26 GHz and 75-110 GHz frequency ranges in a supersonic expansion setup and a room temperature flow cell setup, respectively. The measurements across the 18-110 GHz region enabled the identification and assignment of the vibronic ground state, singly substituted rare atom isotopologues, and vibrationally excited states.

In this work, we report the precise determination of the rotational constants, quartic centrifugal distortion constants, as well as the nitrogen nuclear quadrupole coupling constants for the vibronic ground state. The rotational spectroscopy study of 2,4,6-CHT-1-CN presented here forms the basis for a future astronomical detection of this molecule. Further, the molecule was also subjected to the high voltage electrical discharge source in order to investigate its chemistry under harsh energetic conditions. The analysis of the electrical discharge experiment can provide information on the newly formed molecular species via fragmentation and recombination processes during the electrical discharge experiment.

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Session H

Invited lectures

September 1, Thursday, 8:30 – 10:00

The dance of molecules during the formation of solar-like planetary systems

Cecilia Ceccarelli

Institut de Planétologie et d'Astrophysique de Grenoble (IPAG)
Université Grenoble Alpes, CNRS, France, cecilia.ceccarelli@univ-grenoble-alpes.fr

Planetary systems similar to our own Solar System are born from clumps of molecular clouds in the Milky Way. Subject to the gravitational force, these clumps hugely evolve with time passing through various phases: (1) the prestellar phase, characterised by very low temperatures, ~10 K; (2) the Class 0 and I protostellar phase, where matter is warmed up to ≥100 K; (3) the protoplanetary disk and then (4) the final phase of residual interplanetary matter dispersion. During this evolution, the gas chemical composition changes from simple to large molecules, which become particularly abundant in the protostellar phases.[1, 2] A typical example of the molecular richness observed in solar-like protostars is shown in Fig. 1.

The latest astronomical observations show that planets, asteroids and comets start forming already during the protostellar phase, which implies that chemical content of the former is strongly linked to that of the latter.

In this presentation, I will give a review of the molecules present in the different phases of the forming Solar-like planetary systems and I will show the huge diagnostic power of these molecules to reconstruct not only the present chemical composition but also the past history of the system and maybe its future.

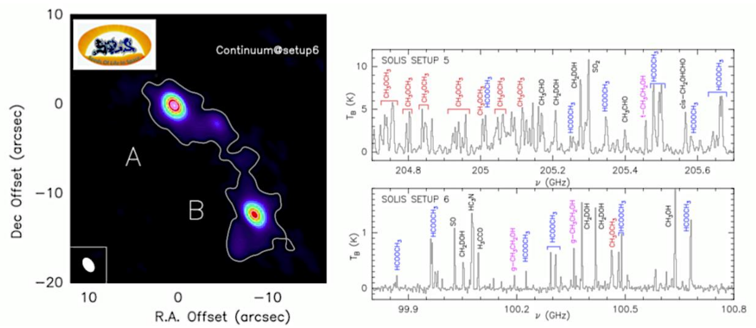

Fig. 1: Image (left panel) of the hot corino of the Class I protostar NGC1333-SVS13 (Bianchi et al., in preparation) and the spectrum (rightpanel) in the millimeter obtained by the IRAM/NOEMA Large Program SOLIS (Seeds Of Life In Space). [3]

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Title: Excited electronic states of YbOH

Timothy C. Steimle[1], Allan Adam[2], Colan Linton[2], Phelan Yu[3], Nicholas R. Hutzler[3]

[1]School of Molecular Science, Arizona State University, USA, TSteimle@ASU.edu; [2]Physics Department, University of New Brunswick, Canada, Colan.Linton@unb.ca; [3]Division of Physics, Mathematics, and Astronomy, California Institute of Technology, USA, hutzler@caltech.edu;

Kozyryev and Hutzler[1] were first to describe the experimental advantages of linear polyatomic molecules relative to a diatomic molecule for investigation of physics beyond the Standard Model (BSM). Signatures of BSM physics include the electron electric dipole moment (eEDM) and/or the nuclear magnetic quadrupole moment (nMQM) determinations. A laser cooled and trapped YbOH sample would be highly advantageous for eEDM and nMQM measurements. As an initial step towards this goal, one-dimensional laser cooling of ^{174}YbOH was recently demonstrated[2] using the closely spaced $P_1(1)$ and $Q_{12}(1)$ lines of the $0_0^0\tilde{A}^2\Pi_{1/2}-\tilde{X}\,^2\Sigma^+$ band[3,4] ($\nu\approx17323$ cm^{-1}) for the main photon cycling transitions. As with the case of the more thoroughly studied YbF[5], laser cooling schemes can become difficult if there are low-lying electronic states arising from excitation of the filled inner-shell 4*f*-electrons. These $4f^{13}$ excited states can strongly perturb the $\tilde{A}^2\Pi_{1/2}$ state used for optical cycling and/or may lie well below the $\tilde{A}^2\Pi_{1/2}$ introducing leaks out of the cycling mechanism via laser induced fluorescence (LIF). Here we report the characterization of the $[17.73]1/2$ and $[18.58]3/2$ states from the high-resolution analysis of the $[17.73]1/2-\tilde{X}\,^2\Sigma^+(0,0,0)$ and $[18.58]3/2-\tilde{X}\,^2\Sigma^+(0,0,0)$ bands which reveals that the these states have significant $4f^{13}$ configuration contributions. The results of survey LIF scans to the blue of the previously reported 17300−17950 cm^{-1} range[6] will also be described.

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Session I

Contributed lectures

September 1, Thursday, 10:30 – 12:00

Observing the Completion of the First Solvation Shell of Carbon Dioxide in Argon from Rotationally Resolved Spectra

A.J. Barclay,[1] A.R.W. McKellar,[2] N. Moazzen-Ahmadi [1]

[1]*Department of Physics and Astronomy, University of Calgary, 2500 University Drive North West, Calgary, Alberta T2N 1N4, Canada,* ajbarcla@ucalgary.ca; [2]*National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada,* bob.Mckellar@gmail.com; [1]*Department of Physics and Astronomy, University of Calgary, 2500 University Drive North West, Calgary, Alberta T2N 1N4, Canada,* nmoazzen@ucalgary.ca

There have been a number of theoretical papers on the structures and energetics of CO_2-Ar_n clusters. But in terms of experiment, the only previous spectroscopic results are for n = 1 (extensive work on the CO_2-Ar dimer) and n = 2 (microwave and infrared spectra of CO_2-Ar_2). We have now obtained and analyzed infrared spectra in the CO_2 ν_3 region for a number of clusters in the range n = 3 to 17. Here we focus on the largest of these, CO_2-Ar_{15} and CO_2-Ar_{17}, which mark completion of the first solvation shell for CO_2 in argon. These clusters have highly symmetric structures with D_{3h} and D_{5h} symmetry, respectively, in good agreement with theory. For n = 15, CO_2 is surrounded by five argon rings, each containing three Ar atoms. For n = 17, there are three rings of five atoms each, plus one Ar atom located on the symmetry axis at each end. The observed spectra are symmetric top parallel bands, and both exhibit distinct intensity alternation which helps to confirm their assignment. Precise values are determined for rotational parameters, and for shifts of the CO_2 vibrational frequency induced by the argon atoms. The spectra indicate possible low frequency (≈ 2 cm^{-1}) vibrational modes in these clusters, posing a challenge for future cluster theory.

Dual-comb mid-infrared spectroscopy with 10^{-4} cm^{-1} wavenumber accuracy and µs time-resolution

Jakob Hayden[1], Olivier Browet[2], Jean Clément[2], Bastien Vispoel[2], Josef A. Agner[3], Sieghard Albert[3], Urs Hollenstein[3], Karen Keppler[3], Pitt Allmendinger[1], Frédéric Merkt[3], Martin Quack[3], Muriel Lepère[2] and Markus Mangold[1]

[1]IRsweep AG, 8712 Stäfa, Switzerland; jakob.hayden@irsweep.com

[2]Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), B-5000 Namur, Belgium;

[3]Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093 Zürich, Switzerland;

The IRis-F1 is a table-top spectrometer based on quantum cascade laser (QCL) dual-comb spectroscopy that covers the important fingerprint spectral region from 900 cm^{-1} to 2200 cm^{-1}. The newly implemented step-sweep technique allows recording spectra at both, high spectral- and time resolution. By step-wise tuning of the center frequency of the combs (interleaving), the spectral sampling can be improved to 2×10^{-4} cm^{-1}. The changes in optical frequency during every step are measured directly from the heterodyne spectrum, yielding an accurate frequency axis.

We present a thorough characterization of the spectrometer in measurements of the ν_1 band of N_2O and ν_4 band of CH_4 between 1283 cm^{-1} and 1333 cm^{-1} [1]. A comparison of the found N_2O line-positions with the HITRAN 2020 database revealed a wavenumber uncertainty of $< 4\times10^{-4}$ cm^{-1} (compare Figure 1a [1]). Doppler-limited measurements of CH_4 showed no systematic broadening of the Gaussian line-shapes, indicating an instrument response function well below 1 MHz (3×10^{-5} cm^{-1}).

We further present high-resolution spectra of CF_4 and $CHCl_2F$ measured in a pulsed, skimmed supersonic beam [2]. Spectra in the 1200 – 1290 cm^{-1} range were recorded with a time-resolution of 4 µs, which allows measuring the evolution of rotational temperature during the gas pulse based on the intensities of ro-vibrational transitions of different rotational quantum numbers (compare Figure 1b, [2]).

Combining 10^{-4} cm^{-1} spectral resolution and µs time resolution, the IRis-F1 is ideally suited for mid-IR spectroscopic studies of both, stable and transient molecular gases.

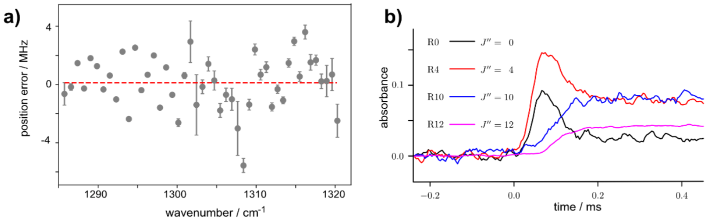

Fig. 1: a) deviation of measured line-positions of N_2O from HITRAN reference values [1]. b) evolution of ro-vibrational transitions of CF_4 in a pulsed molecular beam [2].

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Buffer Gas Cooling and High-Resolution Molecular Spectroscopy at UCLouvain

A. Libert[1], S. Robert[1,2], B Fabre[3], R. Glorieux[1], M. Daman[1], G. Vanlacker[1], B. Hays[1], A. Roucou[1,4], C. Lauzin[1]

[1]*Université Catholique de Louvain, Louvain-la-Neuve, Belgium*

[2]*Planetary Aeronomy, Royal Belgian Institute for Space Aeronomy, 3 Avenue Circulaire, 1180 Brussels, Belgium*

[3]*Université de Bordeaux, CNRS, CEA, CELIA, UMR5107, F33405 Talence, France*

[4]*Université du Littoral Côte d'Opale, Dunkirk, France*

We will report on the development of a cavity ringdown spectrometer coupled to a buffer gas cooling cell reaching 15 K.
We will present the first spectral signature of methanol recorded with this set-up in the overtone range. The evaluation of the temperatures of rotation and translation will be detailed and different perspectives associated to this experimental apparatus will be presented as the use of other home built light sources (ECDL, mode-locked Ti:Sapphire laser), spectrometers (chirped pulse Fourier transform spectrometer) or the possible production of exotic molecular species.

Algorithms for tackling the conformers of flexible molecules

Antonio Fernández-Ramos

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS),
Universidade de Santiago de Compostela, Spain, qf.ramos@usc.es

In recent years, flexible molecules are becoming a frequent target of spectroscopic studies. For these systems, the spectral assignments may be arduous due to the presence of multiple structures, as conformational freedom is one of the main issues when dealing with molecules that present internal rotors. Computational Chemistry can help in this effort by providing the equilibrium structures (conformations) of the molecule, as well as their calculated properties.

However, searching for all conformations of a molecule with several internal rotations is not an easy task. In this work, we present a combined algorithm that merges preconditioned and stochastic searches. The preconditioned method resembles a systematic exploration based on chemical knowledge, whereas the stochastic search is random. These two searching approaches need to be tuned to become fast and efficient. To accelerate the search, a dual-level approach is employed, that is, an initial mapping of the torsional potential energy surface at a low level of theory followed by a further refinement at a high level. The efficiency is associated with the ability of the algorithm to sample extensive regions of the torsional phase-space by avoiding repetitions of already mapped areas. This can be achieved by integrating a series of validation tests that avoid redundancy, as well as the automatic incorporation of torsional enantiomers (if any) to the total number of conformers.

Torsiflex is a Python 3 code developed in our research group and freely distributed at https://github.com/cathedralpkg/TorsiFlex that automatically incorporates the above features. The program can read the SMILES code or the Cartesian coordinates of the molecule. It builds the geometry in internal coordinates and automatically identifies the torsional degrees of freedom. Initially, Torsiflex performs a preconditioned search followed by a stochastic search. This random exploration, by the action of a similarity test, sidesteps the regions of the potential energy surface previously scanned.

Recently, the program was employed to obtain the conformations of each of the twenty proteinogenic amino acids. it was able to locate and characterize a total of 6508 equilibrium structures, a number that almost doubles the amount of previously reported conformers. Additionally, Torsiflex can provide multi-structural harmonic-oscillator partition functions and the contribution of each individual conformer to it as a function of temperature.

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Ab Initio Solution of the Vibration-Rotation Problem with Watson Hamiltonian by Van Vleck Operator Perturbation Theory

Xuankhao Chang[1], **Sergey V. Krasnoshchekov**[1]

[1]*Department of Chemistry, Lomonosov Moscow State University, Russian Federation,*
chang@phys.chem.msu.ru

Among the major approaches for modelling of vibration-rotation energy / IR intensity line lists, the direct problem is often solved by the variational method (VM) while the inverse problem is typically solved by adjusting sets of spectroscopic constants participating in analytic effective Hamiltonians (EH). The VCI method is very efficient for small molecules but requires a subtle empirical correction of *ab initio* data. The EF method is efficient as well, but the choice of adjustable parameters is somewhat equivocal and typically suffers by strong correlations.

A meaningful alternative to VM or EF approaches is the solution of the vibration-rotation problem with Watson Hamiltonian by means of applying the operator version of the canonical Van Vleck perturbation theory (CVPT) in the second, fourth or even higher orders.[1-3] Although the straightforward implementation of CVPT depends on the quality of *ab initio* potential energy and dipole moment surfaces and is less reliable than VM for strongly excited states and large amplitude motions, it has much better scaling properties and produces unambiguous sets of spectroscopic constants than can be further adjusted via EH method. This is very convenient as parameters with linear dependencies within EF model can be fixed. Moreover, such ab initio estimation of adjustable EF parameters can be served as a reliable guide.

In this work, we employed a practical and efficient theoretical approach based on normal ordering of arbitrary products of rotational operators with reducing them to a sum of products $J_z^a J_+^b J_-^c$. For evaluation of vibration-rotation IR intensities a similar procedure is applied for obtaining normally ordered similar products of both direct cosine and rotational operators. As the result, all necessary commutators within CVPT and subsequent evaluation of unitary transformed dipole moment operators can be evaluated. This theoretical scheme is implemented in fast Fortran 95 code ANCO in numerical-analytic form. For treating larger molecules this code can be parallelized.

The efficiency of ANCO code is demonstrated by juxtaposition of modelled spectra of SO_2 molecule with HITRAN data and by comparing spectroscopic constants with literature data.

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A global RAM method for fitting asymmetric tops with one methyl internal rotor and two ^{14}N nuclei: application of the BELGI-2N code to the microwave spectra of methylimidazole isomers.

Nguyen H. V. L.[1], Kleiner I.[2], Schwell M.[1], Gougoula E.[3], Walker N.[4]

[1]Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France,
Lam.Nguyen@lisa.ipsl.fr; Martin.Schwell@lisa.ipsl.fr;
[2] Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France,
Isabelle.Kleiner@lisa.ipsl.fr;
[3]Photon Science - Spectroscopy of Molecular Processes, Deutsches
Elektronen-Synchrotron DESY, Hamburg, Germany, eva.gougoula@desy.de
[4]School of Natural and Environmental
Sciences, Newcastle University, Newcastle-upon-Tyne, UK, nick.walker@newcastle.ac.uk

A number of internal rotation codes can deal with the combination of one or two internal rotor(s) with one ^{14}N quadrupole nucleus, but not many treat the internal rotations with two ^{14}N nuclei. Here we present the extended version of our internal rotor program (BELGI-Cs), called BELGI-2N using the Rho-Axis Method (RAM)[1], a global approach to deal with the compounds containing one methyl top and two weakly coupling ^{14}N nuclei. For molecules containing a ^{14}N nucleus with a nuclear spin I equal to 1, all rotational transitions of the rigid rotor split into several hyperfine components. The quadrupole moment is relatively small and can be treated using a first order perturbation approximation.

To test our new code, we applied it to the microwave data previously recorded for N-, 2, 4- and 5-methylimidazole, using a chirped-pulse Fourier transform microwave spectroscometer in the 7.0–18.5 GHz frequency range[2]. Compared to this study, we were able to perform global fits with root-mean-square deviations within the experimental accuracy and to increase the number of assigned lines with the high predictive power of the fits.

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Session IMM

8th Ioannes Marcus Marci

September 1, Thursday, 16:20 – 18:00

Ultrasensitive spectroscopy: from microcavities to satellites

David A. Long[1]

[1]*National Institute of Standards and Technology, USA david.long@nist.gov*

Our laboratory leverages recent developments in optical cavities and optical frequency combs to perform highly accurate measurements of atomic and molecular species as well as to perform physical metrology. These efforts span a wide variety of length scales from macroscale optical cavities near a meter in length to cavity optomechanical devices with lengths of only a few hundred micrometers.

On major effort in our group is to utilize novel cavity ring-down spectroscopy methods to produce high accuracy line shape parameters for atmospherically relevant species. Much of this work is done to enable retrievals of greenhouse gas concentrations from satellite and ground-based remote sensing platforms. Recently, we have demonstrated line intensity uncertainties below 0.1% for carbon dioxide[1] as well as transition frequency uncertainties near 200 Hz.[2] These measurements have been enabled by high finesse optical cavities, linkage to a self-referenced optical frequency comb, and electro-optic-modulator-based rapid scanning approaches.[3]

Further, we have been developing devices and methods for the use of cavity optomechanical devices for high accuracy acceleration measurements. These devices contain few-hundred-micron-long Fabry-Pérot optical cavities in which one of the mirrors is suspended on a series of narrow beams. This allows for readily observable cavity length changes in the presence of external acceleration. We have demonstrated thermomechanically noise limited performance with sensitivities near 30 ng/Hz$^{1/2}$.[4] Finally, we have developed electro-optic frequency comb approaches for rapid interrogation of the cavity displacement, allowing for dramatically improved dynamic range.[5]

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Molecular spectroscopy of chirality recognition/transfer/ amplification: fundamental and practical advances

Yunjie Xu

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2
yunjie.xu@ualberta.ca

A molecule is chiral if its mirror image cannot be superimposed onto itself. Chirality serves an essential function in life. Our research program centres on understanding mechanisms of chirality recognition/transfer/amplification at the molecular level. To achieve this goal, we apply and develop new spectroscopic tools to characterize structural and dynamical properties of chiral molecules and non-covalent interactions among them in the gas phase, solution, cold rare gas matrices and at liquid-liquid interfaces.

We emphasize the connection between the gas phase results obtained using high resolution spectroscopy and the condense phase results using several chiroptical spectroscopies. For example, we examined the conformational landscapes of tetrahydro-2-furoic acid and its aggregates using jet-cooled chirped pulse Fourier transform microwave spectroscopy, matrix isolation and solution vibrational circular dichroism spectroscopy.[1] The connection between these studies and the practical application of chiral tag spectroscopy[2] will be discussed. We also evaluated large amplitude motions in the binary adduct of water and 1-phenyl-2,2,2-trifluroethanol, a chiral alcohol, and used this result to highlight the challenges in modeling water solvation effects in chiroptical measurements.[3]

While carrying out Raman optical activity (ROA) measurements of several transition metal complexes under resonance, very strong chiral Raman signals of achiral solvents were detected. The search for the possible mechanisms let us to the discovery of a new form of chiral Raman spectroscopy, i.e., eCP-Raman.[4] eCP-Raman combines two spectroscopies into one: electronic circular dichroism and circularly polarized Raman (CP-Raman).[3] In addition, we showed how to quantify eCP-Raman contributions and to extract true resonance ROA signals, providing crucial experimental data for the development of resonance ROA theory.

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Session J

Contributed lectures

September 2, Friday, 8:30 – 10:20

Dual-comb cavity ring-down spectroscopy

Daniel Lisak[1],*, Dominik Charczun[1], Akiko Nishiyama[1,2], Thibault Voumard[3], Thibault Wildi[3], Grzegorz Kowzan[1], Victor Brasch[4], Tobias Herr[3,5], Adam J. Fleisher[6], Joseph T. Hodges[6], Roman Ciuryło[1], Agata Cygan[1], Piotr Masłowski[1]

*[1]Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń,ul. Grudziądzka 5, 87-100 Toruń, Poland; [2]National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan; [3]Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany; [4]CSEM - Swiss Center for Electronics and Microtechnology, 2000 Neuchâtel, Switzerland; [5]Physics Department, Universität Hamburg UHH, Luruper Chaussee 149, 22761 Hamburg, Germany; [6]Optical Measurements Group, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA; *email: dlisak@umk.pl;*

Cavity ring-down spectroscopy is a well-recognized method for many research fields involving light-matter interactions because of its, high resolution, sensitivity, accuracy and simplicity. In the first 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, we show consistency between the retrieved absorption and dispersion spectra. Our DC-CRDS technique combines 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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Doppler-free absorption and dispersion saturation spectroscopy of carbon monoxide

Szymon Wójtewicz, Katarzyna Bielska, Agata Cygan, Magdalena Konefał, Grzegorz Kowzan, Mikołaj Zaborowski, Dominik Charczun, Piotr Wcisło, Piotr Masłowski, Roman Ciuryło, Daniel Lisak

Institute of Astronomy, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, ul. Grudziądzka 5, 87-100 Toruń, Poland, szymon@umk.pl

Measurements of the absolute frequency of atomic and molecular transitions are the most sensitive tools for, among others, fundamental studies and optical metrology. Here we present an accurate determination of the positions of the carbon monoxide (3-0) band transitions using the Doppler-free saturated-absorption or dispersion spectroscopy. We applied three ultra-sensitive cavity-enhanced techniques: the well-established cavity ring-down spectroscopy (CRDS), the cavity mode-width spectroscopy (CMWS)[1], and the cavity mode-dispersion spectroscopy (CMDS)[2,3]. The last two techniques were employed for the first time for the Doppler-free saturation spectroscopy[4]. The frequency-based CMDS method is advantageous to the other two intensity-based ones. It enables measurements in broader pressure range and shows high immunity of the Lamb dip position to the simplifications in the model of saturated cavity mode shape as well as saturating power variations. The unperturbed transition frequencies are determined with standard uncertainties below 500 Hz, translating to relative uncertainties below $3x10^{-12}$. Contrary to the literature data[5], we detect non-zero pressure shift of transitions under investigation in saturation conditions.

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The Rotationally Resolved IR Spectrum of Diatomic Vanadium Oxide

Eileen Döring[1], Luisa Blum[1], Alexander A. Breier[1], Thomas F. Giesen[1], Guido W. Fuchs[1]

[1]University of Kassel, Institute of Physics, Heinrich-Plett Str. 40, 34132 Kassel, Germany,
corresponding address: eileendoering@physik.uni-kassel.de

Small molecules made of refractory materials are thought to play an important role in the dust formation processes around late-type stars. Likewise, they take part in the opacity process of variable late-type stars, as has been shown for the molecule TiO.[1]
Because of similar formation conditions, the diatomic molecule vanadium oxide (VO) is thought to occur in similar locations around stars as TiO.[2]
VO has already been detected in the near-infrared region in the envelope of the red hypergiant VY CMa[3], but due to the lack of high-resolution laboratory spectra, no astrophysical search of VO in the mid-IR region has been performed.
In this work, we report the ro-vibrational absorption spectrum of $X^4\Sigma^-$ VO, including its hyperfine structure.
In our experiment we used a frequency modulated quantum cascade laser in combination with Herriott-type multipass optics. The molecules were produced by laser ablation of a vanadium rod and a N_2O/He buffer gas, which was subsequently adiabatically expanded into a vacuum chamber. The rotationally cooled spectrum was analysed using the Pgopher software and the molecular constants were determined.
The experimental data as well as line predictions will enable a dedicated search for this molecule in space at mid-IR wavelengths.

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Accurate data for infrared ammonia spectra: the 4700-5650 cm^{-1} range

Peter Čermák[1], Odřej Votava[2], Jozef Rakovský[2], Patrice Cacciani[3], Jean Cosléou[3], Alain Campargue[4], Jean Vander Auwera[5]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovakia, cermak@fmph.uniba.sk; [2]Heyrovský Institute of Physical Chemistry, Dolejškova 2155/3, Prague 8, 18223, Czech Republic; [3]Laboratoire de Physique des Lasers, Atomes et Molécules, CNRS, UMR 8523 Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France; [4]UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France; [5]SQUARES, Université Libre de Bruxelles, Brussels, Belgium

Accurate reference laboratory data represents a key element for understanding any remote observations in particular astrophysical surveys. A recent high resolution FTS absorption spectrum [1] motivates the interest of new analysis with the help of high accurate ab initio calculations [2]. The 4700-5650 cm^{-1} range fills the hole of our previous works for the 3900-4700 [1] and the 5650-6350 cm^{-1} [3] ranges. The lower state combination difference technique is very powerful with such accurate spectrum as well as the ability of the ab initio calculation to reproduce position and intensity of the transitions. However, this is upset in the case of quasi degenerated energy levels and yields for the transitions to a transfer of intensity. This phenomenon has been systematically explored in this work and should be considered in future work, particularly for higher energy ranges.

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Global analysis of the large amplitude motion in propylene oxide

Vávra K.[1], Döring E.[1], Jakob J.[1], Peterß F.[1], Fuchs G. W.[1], Stahl P.[1], Kaufmann M.[1], Vereijken A.[1], Schlesag M.[1], Giesen T. F.[1]

[1]*Institute of Physics, University of Kassel, Kassel, Germany*

Propylene oxide, $CH_3C_2H_3O$, is a stable chiral molecule that gained new attention through its recent radio astronomical discovery in the interstellar medium toward the galactic center[1]. Subsequently, extensive laboratory data on rotational transitions in the ground state and in the lowest vibrationally excited ν_{24} torsion state have been published[2,3]. Previously, only the 3 μm spectral range of the four C-H stretching modes was partially observed with high spectral resolution at mid-infrared wavelengths[4].

The present study aims to understand some effects of large amplitude motions, particularly the coupling of the internal rotation of the methyl top to different vibrational modes. The effects in a perturbed triad consisting of the second torsional excited state $\nu_{24} = 2$ and the two CH_3 bending modes $\nu_{23} = 1$ and $\nu_{22} = 1$ were observed in millimetre-wave spectrum. Line splitting due to internal rotation of the methyl group in a triple-well potential was also observed in the mid-infrared region at 8 and 10 μm for the ν_{12} ring breathing mode and the ν_{17} excited state (CH_2 rock), respectively. An extended scan of the range of C-H stretching vibration modes at 3 μm is still in progress. All spectra were analysed by several graphical techniques such as Loomis-Wood diagram, Savitzky-Golay smoothing, line fitting and assignment, spectral simulation. For this, a homemade program written in Python code was produced. For the spectral prediction as well as for the determination of molecular parameters we used the SPFIT/SPCAT program package[5] and XIAM[6].

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Multiple Water Configurations in Fenchone-$(H_2O)_{1-7}$ Hydrates Revealed by Rotational Spectroscopy

Ecaterina Burevschi[1], Mhamad Chrayteh[2], Donatella Loru[1], S. Indira Murugachandran[1], Pascal Dréan[2], M. Eugenia Sanz[1]

[1]Department of Chemistry, King’s College London, London SE1 1DB, UK,
ecaterina.burevschi@kcl.ac.uk, donatella.loru@desy.de,
seema.murugachandran@kcl.ac.uk,maria.sanz@kcl.ac.uk;

[2]PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France, pascal.drean@univ-lille.fr, mhamad.chrayteh@univ-littoral.fr

Fenchone is a bicyclic monoterpenoid that is released to the atmosphere by natural and anthropogenic sources, where it interacts with other atmospheric molecules such as water. Here we present the investigation of the hydrates of fenchone $C_{10}H_{16}O\cdots(H_2O)_n$ (n = 1-7) by microwave spectroscopy, in the frequency range 2 to 20 GHz, and computational calculations[1]. Several isomers of each hydrated complex have been observed and their rotational and centrifugal distortion constants determined. For fenchone$\cdots(H_2O)_{1-4}$ complexes, observation of the ^{18}O isotopologues allowed us to determine the location of the oxygen atoms of water and the configuration of water molecules around fenchone. Water binds to fenchone through O–H···O and C–H···O hydrogen bonds. In the mono-, di- and trihydrates water molecules arrange in open chains around fenchone, while for the higher order hydrates water molecules adopt distorted tetramer, pentamer and hexamer configurations. The various configurations as well as the relevant intermolecular interactions, and their modelling by computational methods, will be discussed.

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Session K

Contributed lectures

September 2, Friday, 10:40 – 12:30

R(0) and R(1) rotational lines of the CO molecule in Ar bath: experimentally measured collisional parameters versus *ab initio* calculations

Aleksandr A. Balashov[1], Mikhail Yu. Tretyakov[1], Evgeny A. Serov[1], Dmitriy S. Makarov[1], Ilya N. Vilkov[1], German Yu. Golubyatnikov[1], Tatyana A. Galanina[1], Maksim A. Koshelev[1], Anna A. Simonova[2], Franck Thibault[3]

[1]Institute of Applied Physics, Russia, balashov@ipfran.ru; [2]V.E. Zuev Institute of Atmospheric Optics, Russia; [3]Univ Rennes, CNRS, Institut de Physique de Rennes, France

We present the results of a rigorous study of the two first pure rotational transitions of carbon monoxide perturbed by Ar. Measurements are done on three different by principle of operation spectrometers with complementary abilities covering pressure range from 0.02 up to 1500 Torr. This approach allows not only to cover this wide pressure range but also to carefully account for the systematic instrumental-related effects, which can bias the retrieved line shape parameters values.

The measurements of collisional line shape parameters are supported by fully *ab initio* calculations, which are in remarkable agreement with retrieved data. A sub-percent uncertainty of line intensity measurements is achieved, and the first firm evidence that the resonance spectrum of CO is observed on the continuum pedestal is given. We analyze the results of *ab initio* calculations on the basis of early analytical theories and demonstrate the good general applicability of the latter to the CO-Ar collisional system[1]. The study is supported by RSF project 22-17-00041.

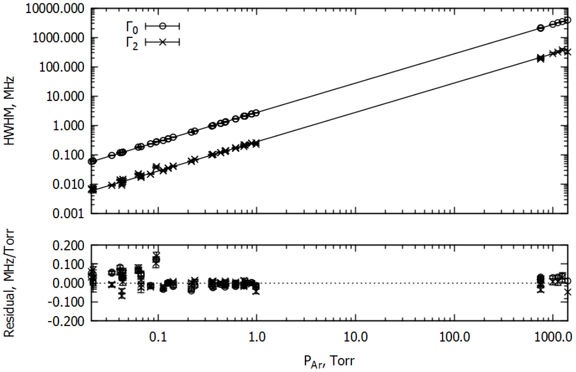

Fig. 1: Dependence of the R(0) speed-dependent HWHM parameters Γ_0 and Γ_2 versus Ar partial pressure (solid lines show the result of the linear regression).

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Title: The hydration of polycyclic aromatic compounds: the case of naphthaldehyde

Jordan A. Claus[1*], Celina Bermúdez[1,2], Manuel Goubet[1], Laurent Margulès[1]

[1] Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France
[2] Departamento de Química Física y Química Inorgánica, Facultad de Ciencias - I.U. CINQUIMA, Universidad de Valladolid, Valladolid 47011, Spain

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, α- and β-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. Both isolated α- and β-naphthaldehyde species could present two possible structures: *cis,* the most stable one for α, and *trans* for β.[2] Our calculations show that there are three low energy monohydrates predicted for each conformer, *cis*/*trans*, in an energy range of 1500 cm^{-1}. Experimentally, one conformer has been observed in gas phase for α and two for β, corresponding to the calculated most stable structures. All species are stabilized by intermolecular hydrogen bonds between the water molecule and the aldehyde group of naphthaldehyde: for the α isomer, the oxygen of the aldehyde acts as proton acceptor and the aldehyde hydrogen as proton donor; for the β isomer, the oxygen of the aldehyde acts as proton acceptor and one of the ring hydrogens as a proton donor.[3]

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* correspondant : jordan.claus@univ-lille.fr

Microsolvation vs droplet aggregation: A broadband rotational spectroscopic study of 3-methylcatechol water complexes

Arsh Hazrah[1], Aran Insausti[1,2], Jiarui Ma[1], Mohamad Al-Jabiri[1], Yunjie Xu[1], Wolfgang Jäger[1]

[1]*University of Alberta, Canada, hazrah@ualberta.ca;* [2]*Universidad del País Vasco, Spain*

Biomass burning greatly influences the Earth-cloud-climate system by releasing complex mixtures of organic and inorganic species into the atmosphere.[1] During biomass burning, lignin, an organic polymer and a major component of wood[2], undergoes pyrolysis resulting in the direct release of substituted catechols,[3] which contribute to the formation of secondary organic aerosol.[4] 3-methylcatechol (3MC), a common substituted catechol, may be photo-oxidized or aggregates with other atmospherically relevant molecules, such as water, forming small molecular clusters or hydrates. These hydrates play an important role in the early phases of aerosol particle formation, and can provide valuable thermodynamic data for modelling.

To elucidate the conformationally complex hydrate structures we analyzed rotational spectra measured with a chirped-pulse Fourier transform microwave spectrometer in the 2-6 GHz range.[5] To aid in the spectral assignment, we used the Conformer–Rotamer Ensemble Sampling Tool (CREST)[6] to generate an ensemble of conformers. Two monomer conformations with their respective ^{13}C isotopologues were assigned, followed by the determination of substitution structures and so-called semi-experimental effective structures. With the aid of the CREST results, transitions of several hydrates, 3MC-$(H_2O)_{n=1-4}$, were also assigned in the experimental spectrum. For the monohydrate and dihydrate, splitting of rotational transitions into quartets were observed. These splittings are a consequence of the methyl internal rotation (MIR) and the proton exchange of the water molecule. MIR splittings are still present for the trihydrate, but a splitting pattern attributable to the proton exchange motion is no longer observed. No MIR or proton exchange splitting is present for the tetrahydrate. Non-covalent interactions[7] and natural bond orbital analyses[8] were used to visualize and quantify the intermolecular interactions within each cluster.

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σ-hole activation and structural changes upon perfluorination of aryl halides: direct evidence from gas phase rotational spectroscopy

Sonia Melandri,[1] Assimo Maris,[1] Luca Evangelisti,[1] Dinding Lv,[1] Wentao Song,[1] Andrea Maggio,[1] Ashley A. Elliott,[2] Sean A. Peebles,[2] Rebecca A. Peebles,[2] Justin L. Neill,[3] Matt T. Muckle, [3] Brooks H. Pate[3]

[1]*Department of Chemistry, University of Bologna, via Selmi, 2 40126 Bologna, Italy,*
sonia.melandri@unibo.it

[2] *Department of Chemistry and Biochemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920, USA*

[3] *Department of Chemistry, University of Virginia, McCormick Rd., PO Box 411319, Charlottesville, VA 22904, USA*

Enhancement of the σ-hole on the halogen atom of aryl halides due to perfluorination of the ring is demonstrated by use of the Extended Townes−Dailey (ETD) model coupled to a Natural Atomic Orbital Bond analysis on two perfluorinated aryl halides (C_6F_5Cl and C_6F_5Br) and their hydrogenated counterparts. The ETD analysis, which quantifies the halogen p-orbitals populations, relies on the nuclear quadrupole coupling constants which are accurately determined experimentally from the rotational spectra. The rotational spectra investigated by Fourier-transform microwave spectroscopy performed in supersonic expansion have been investigated for the parent species of C_6F_5Cl and C_6F_5Br and their ^{13}C, ^{37}Cl or ^{81}Br substituted isotopologues observed in natural abundance. The experimentally determined rotational constants combined with theoretical data at the MP2/aug-cc-pVTZ level and the observed nuclear quadrupole coupling constants reproduced by Douglas-Kroll-Hess second order scalar relativistic calculations provide precise structural information from which an elongation of the ring along its symmetry axis due to perfluorination is proved.[1]

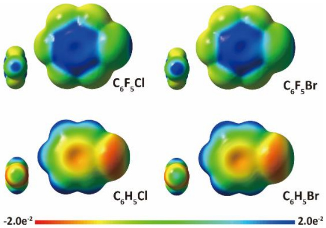

Fig. 1: Electrostatic potential maps of C_6H_5X, C_6F_5X (X=Cl, Br)

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Microwave study of α-pinene-oxide with the new CP-FTMW spectrometer in Lille

Noureddin Osseiran[1], Elias M. Neeman[1], Manuel Goubet[1], Hervé Damart[1],
Gauthier Dekyndt[1], Thérèse R. Huet[1]

[1] *Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France*

The introduction of the chirped-pulsed Fourier transform microwave spectrometer (CP-FTMW) by the group of Brooks Pate[1], was a breakthrough in terms of flexibility, speed and bandwidth, that revolutionized the field of microwave spectroscopy. Here we present a newly constructed CP-FTMW spectrometer operating in the range 6-18 GHz. A fast-arbitrary waveform generator (Keysight M8195A 65 GSa/s) is used to generate the 4 µs chirped pulse. A fast oscilloscope (Keysight DSOZ634A 160 GSa/s) is employed to record the molecular Free Induction Decays (FID). The large memory and high acquisition speed of the oscilloscope permit to record for longer times (up to 80 µs), thus achieving high spectral resolution (FWHM better than 40 kHz). The present setup has been characterized and is used to study molecules of atmospheric interest. The rotational study of α-pinene-oxide will be presented in detail, as well as its geometrical structure, with the support of quantum chemical calculations.

The present work was funded by the Labex CaPPA (ANR-11-LABX-0005-01), by the Regional Council Hauts-de-France, by the European Funds for Regional Economic Development, and by the CPER CLIMIBIO and CPER P4S.

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Conformational study of the synthetic repellents DEET and Picaridin to improve structure-based design of novel mosquito repellents

Otger Crehuet Viladelbosch[1,2], Aran Insausti[1,2], Maider Parra[1,2], Elena R. Alonso[1,2], Emilio J. Cocinero[1,2]

[1] *Physical Chemistry Department, Universidad del País Vasco (UPV/EHU), 48080 Bilbao, Spain*
[2] *Biofisika Institute (CSIC, UPV/EHU), 48080 Bilbao, Spain*

Today, several potentially lethal diseases such as malaria, yellow fever and encephalitis are transmitted by mosquito bites. These insects act as vectors carrying the actual cause of the disease. The best way to prevent them is to keep the transmission vectors away from the population. Here is where repellents come into play. The most effective repellent used worldwide for six decades is *N,N-diethyl-m-toluamide* (DEET)[1]. At the moment, the most promising candidate for a new repellent is *butan-2-yl 2-(2-hydroxyethyl)piperidine-1-carboxylate (Picaridin)*[2]. However, there are some problems with these compounds. Therefore, there is a clear need for a more effective repellent.

In our study we interrogated both *DEET* and *picaridin* using chirped pulse Fourier transform microwave spectroscopy (CP-FTMW)[3]. This way, we have identified and characterized the structure of different gas-phase conformations. We first predicted the structures using computational calculations and latter we recorded the spectrum of the molecules using our home-made spectrometer using 2 nozzles to inject the sample at 1 Hz and recording the spectrum from 7 to 14 GHz for the *DEET* and from 2 to 6 for the *picaridin*. With our data and the one from other studies in complex with macromolecular targets it's possible to find which structural motifs or functional groups dispositions can be exploited to enhance the repellent properties and design new and more efficient repellents.

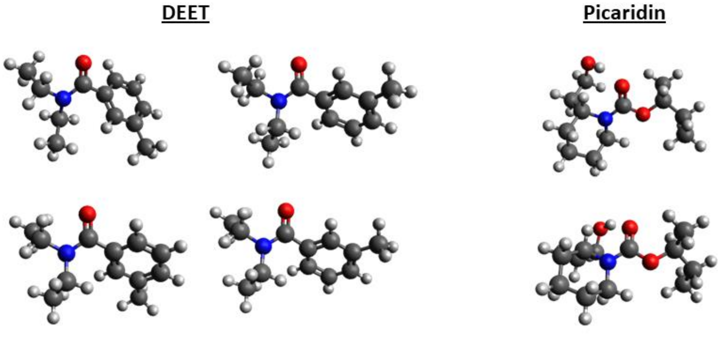

Figure 1: Detected conformations of DEET and Picaridin

References

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[3] I. Uriarte, C. Pérez, E. Cballero-Mancebo, F. J. Basterretxea, A. Lesarri, J. A. Fernández, E. J. Cocinero, *Chem. Eur. J.* **2017**, *23*, 7238–7244.

Title: Microwave study of H_2 in complexes with small aromatic molecules

Robin Dohmen[1], Pablo Pinacho[2], Beate Kempken[1], Melanie Schnell[2], Daniel Obenchain[1]

[1]Georg August University, Göttingen, m.dohmen@stud.uni-goettingen.de; [2]Deutsches Elektron-Synchroton (DESY), Germany, pablo.pinacho@desy.de;

Non-Covalent interactions play a key role in the formation of molecular complexes and reactivity. In previous works only interactions of inorganic and metallic species with hydrogen have be investigated by rotational spectroscopy.[1, 2] The interactions of molecular hydrogen with aromatic systems are unexplored.

In this work the bond of hydrogen to the π-system of halogen benzaldehydes is investigated. These volatile systems possess a large dipole moment and provide a method of increasing the complexity of the system by the introduction of quadrupolar nuceli. The quadrupolar coupling acts as a spectroscopic probe for the electronic field gradient around the nucleus and provides insights into the long-range dispersive interactions. Of particular interest are the differences observed for the rotational spectrum of *ortho*- and *para*-hydrogen and its structural impact investigated by isotopic substitution. The two spin isotopes show significant differences in rotational that demonstrates there are significant differences in binding strength of o-H_2 and p-H_2, which are experimentally observable. Broadband rotational spectra are presented which are supplemented with cavity data to resolve the additional hyperfine splitting of o-H_2 to the total angular momentum of the molecule. These experimental results are directly compared to a number of quantum chemical predictions to benchmark computational methods.

References

[1] W. Jäger, et al., *J. Chem Phys.,* **127**, 054305, 2007

[2] D. Obenchain, H. Frank, H. Pickett, S. Novik, *J. Chem. Phys.*, **146**, 204302, 2017

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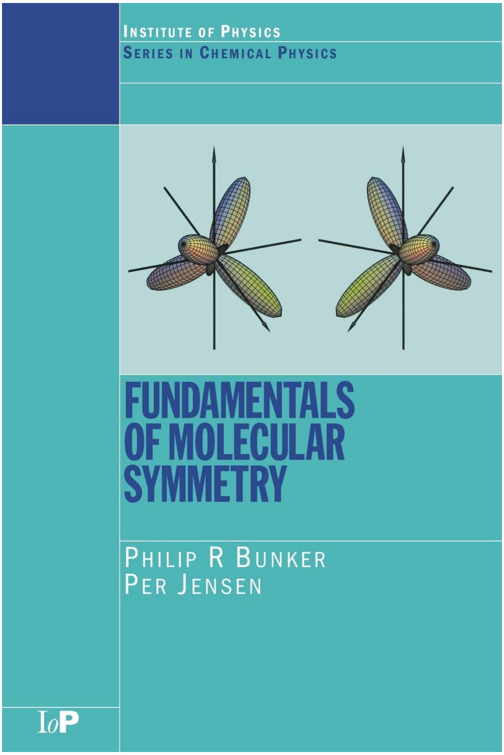
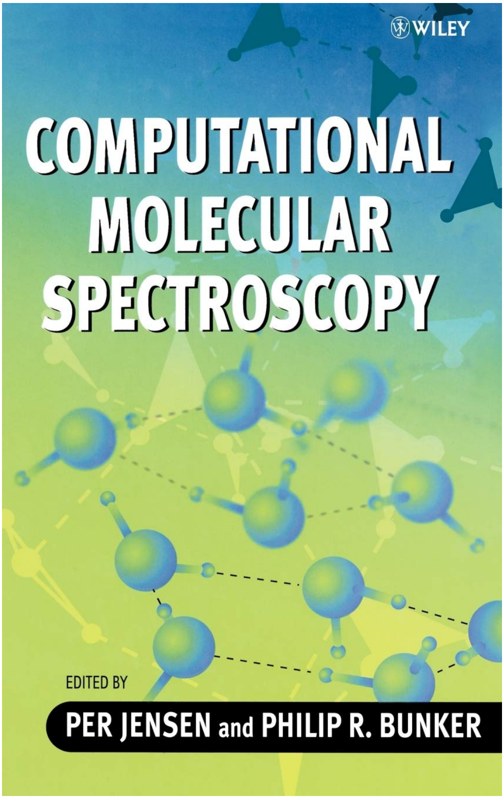


Fundamentals of Molecular Symmetry

by P. R. Bunker and P. Jensen

Winner of a 2005 CHOICE Outstanding Academic Book Award

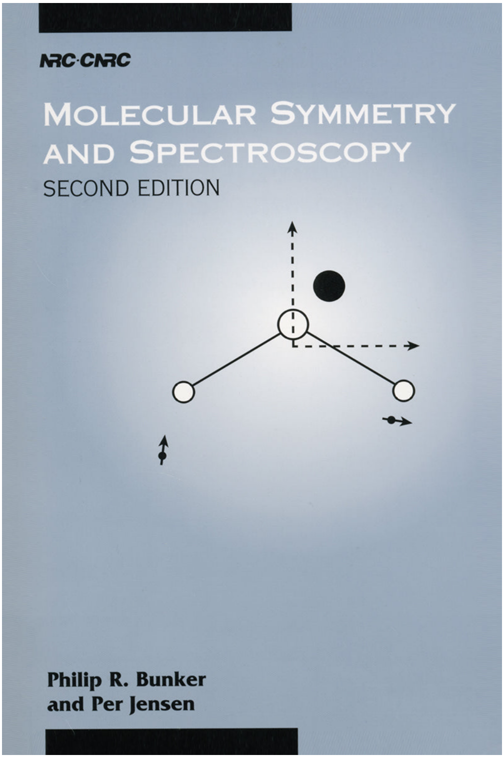
The book provides an introductory description of molecular spectroscopy and quantum mechanics as the foundation for understanding how molecular symmetry is defined and used. The approach taken gives a balanced account of using both point groups and molecular symmetry groups. Usually the point group is only useful for isolated, nonrotating molecules, executing small amplitude vibrations, with no tunneling, in isolated electronic states. However, for the chemical physicist or physical chemist who wishes to go beyond these limitations, the molecular symmetry group is almost always required.



Computational Molecular Spectroscopy

by P. Jensen and P. R. Bunker

The book describes the use of modern computational methods in predicting high resolution molecular spectra, which allows the experimental spectroscopist to interpret and assign real spectra.



Molecular Symmetry and Spectroscopy

by P. R. Bunker and P. Jensen

The textbook explains the use of the molecular symmetry group in understanding high resolution molecular spectra.

Additional information

Addresses:

Conference Site:

University of Chemistry and Technology, Prague

http://www.vscht.cz
Address: Technická 5, 16628 Praha 6,
Metro: line A - Dejvická, Bus 119,
Trams: 8, 18, 20, 26, – Vítězné nám., 20, 26 - Dejvická

Ioannes Marcus Marci Session: The Prague City Hall

Auditorium
https://www.praha.eu/jnp/en/about_prague/city_administration/city_hall/index.html
Address: Mariánské nám. 2., Prague 1,
Metro: line A, Trams: 17, 18 - Staroměstská

Reception: Residence of Lord Mayor of Prague

https://www.prague.eu/en/object/places/2779/the-lord-mayors-residence
Address: Mariánské nám. 1, Prague 1
Metro: line A, Trams: 17, 18 - Staroměstská

Concert: Magna Aula of Carolinum

Historical Grand Auditorium, Charles University,
http://en.wikipedia.org/wiki/Karolinum
Address: Ovocný trh 5, Prague 1
Metro: line A – Můstek, line B – Můstek or Náměstí republiky
Trams 6, 8, 15, 26 – Náměstí republiky

CV of the **Big Band Biskupská**

Conductor: Milan Tolkner

web site: http://bigbandbiskupska.cz/

Big Band Biskupská is one of the largest student music orchestras in Prague. It has performed with František Zahradníček, Tomáš Savka, Václav Noid Bárta, David Uličník, Slava Korsak and Ondřej Ruml.

A permanent singer soloist of the band is Kateřina Tošnarová, ZUŠ Biskupská’s absolvent and a student of Jaroslav Ježek Conservatory.

Big band Biskupská’s frequently rearranged repertoire contains more than 100 pieces of swing, pop, dance, jazz or rock music.

The conductor of the band is Milan Tolkner, a music teacher and a longtime soloist of The Band of the Castle Guards and Police of the Czech Republic.

In 2017, the big band has obtained a golden award diploma at the national ZUŠ jazz orchestra contest in Litvínov.

Access from
Chomutov /
Chemnitz

Conference site
Map #2

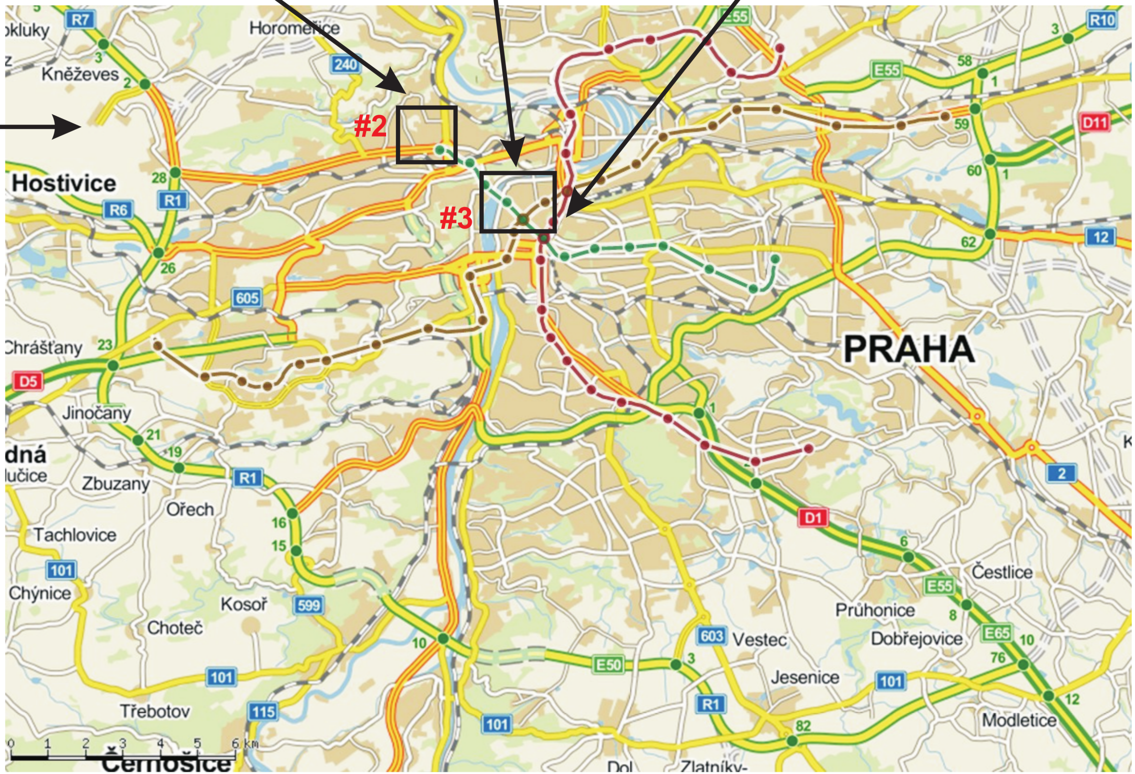
IMM Session / Concert
Map #3

Central railway
station

Access from
Dresden
D8 / E55

Prague airport
Bus 119

Access from
Rozvadov /
Pilsen
E50 / D5



Access from
České Budějovice - R4

Access from Brno - D1 / E50

Map #2 - Conference site

1 - Registration, lecture room, posters
2 - University canteen "Studentský dům"
3 - Sinkule dormitory
4 - Masaryk hotel/ dormitory & restaurant Masaryk dormitory
5 - Dejvická dormitory
6 - Subway station - Dejvická (line A)

Map # 3 - IMM Session and Concert

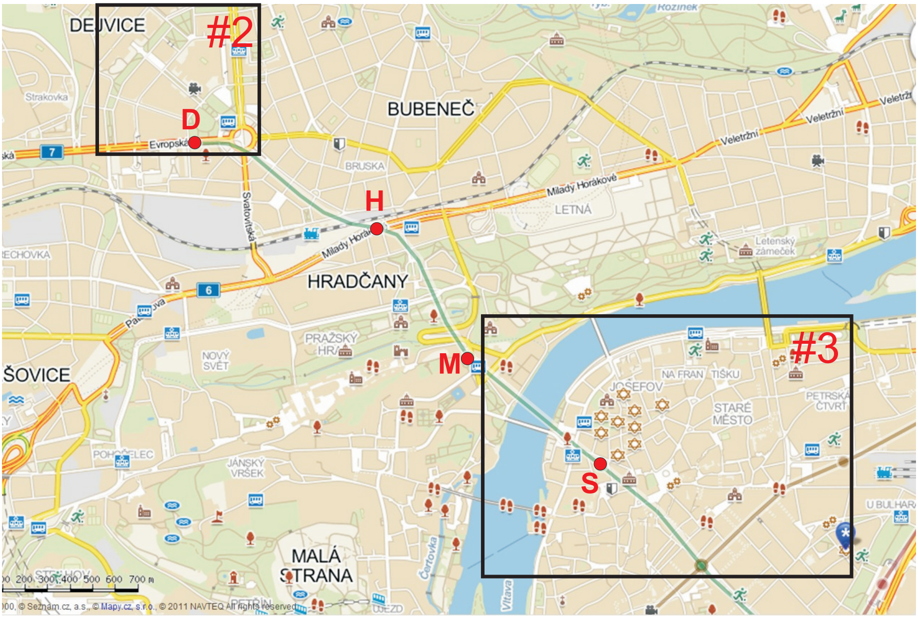
1 - Ioannes Marcus Marcii Session (The Prague City Hall)

2 - Reception (Residence of Lord Mayor of Prague)

3 - Concert (Magna Aula of Carolinum)

S - subway **S**taroměstská (line **A**)
M - subway **M**ůstek (line **A**)
N - subway **N**áměstí republiky (line **B**)

Map # 4 - link between maps #2 and #3



Map # 2 - Conference site

Map # 3 - IMM session and Concert

Subway - line **A**
(**D**ejvická, **H**radčanská, **M**alostranská,
Staroměstská)