BOLOGNA2024

The 27th International Conference on High-Resolution Molecular Spectroscopy
Bologna, Italy, September 2–6, 2024

Book of abstracts and programme

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ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA
DEPARTMENT
OF CHEMISTRY
"GIACOMO CIAMICIAN"

Activity funded with the contribution of the
Department od Excellence program
financed by the Minister of University and Research
2023-2007 (L. 232 del 01/12/2016)

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA
DEPARTMENT
OF INDUSTRIAL CHEMISTRY
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On behalf of the International Steering Committee, the Executive Committee and the Local Organizing Committee I warmly welcome all the participants to the 27th International Conference on High Resolution Molecular Spectroscopy to the University of Bologna.

The conference covers fundamental and applied aspects of high-resolution molecular spectroscopy including a variety of experimental studies, techniques, methods, and theories. Applications in related fields such as the physics and chemistry of the atmospheres of planets and cool stars, the physics and chemistry of the interstellar medium, chemical kinetics, biologically important molecules in the gas phase or in matrices, combustion, cold molecules, metrology are also included.

The vitality and significance of high resolution spectroscopy is proven by the high number of participants and contributions; many of them given by students. The plenary sessions include 10 invited talks while the 3 parallel sessions include 9 keynote talks and 136 contributed talks. The program also includes 2 poster sessions showcasing 98 presentations. As important as the program are the formal and informal discussions and we sincerely hope to provide the right environment for these interactions to thrive.

I express my gratitude to all the Committees members, in particular to the Local Organizing Committee for their help and dedication, and to the participants who accepted to chair the oral sessions and to act as referees for the Student prizes. I also warmly thank all the sponsors and the Department of Chemistry for their financial contributions and the University of Bologna for the support and the availability of the infrastructures.

We wish you a profitable and enjoyable meeting!

Sonia Melandri
Conference Chair

Contents

About

BOLOGNA 2024

The International Conference on High-Resolution Molecular Spectroscopy 2024, part of the Prague Spectroscopy Conference Series, marks the 27th edition of the Conference, extending a history that started biannually in 1970 to bring together spectroscopists from the East and West of Europe and all around the Globe. The powerful scientific program will combine ten invited plenary lectures, and contributed oral and poster presentations, emphasizing the contributions of young researchers.

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Compact Timetable

	Sunday 01/09/24	**Monday 02/09/24**	**Tuesday 03/09/24**	**Wednesday 04/09/24**	**Thursday 05/09/24**	**Friday 06/09/24**
8:45 – 9:00	Arrival	Opening				Student prizes
9:00 – 10:30		MA plenary	Sessions TB1/TC1/TD1	WA plenary	ThA plenary	FA plenary
10:30 – 11:00		Break	Break	Break	Break	Break
11:00 – 12:30		Sessions MB1/MC1/MD1	Sessions TB2/TC2/TD2	Sessions WB1/WC1/WD1	Poster 2	Sessions FB1/FC1/FD1
12:30 – 14:00		Lunch	Lunch	Lunch‡	Lunch	Lunch
14:00 – 16:00		Sessions MB2/MC2/MD2	TA plenary	Free afternoon	Sessions ThB1/ThC1/ThD1	Departure
16:00 – 16:30	Registration Get together†	Break	Break*		Break	
16:30 – 18:30		Sessions MB3/MC3/MD3	Poster 1**		Free time Excursion	
18:30 – 22:30				Concert Social dinner		

† Get together until 19:30; * coffee break at 15:30; ** from 16:00 to 17:30; ‡ lunch at 13:00.

Useful Information

Venue

Talks and **poster sessions** will be held at teaching building — Complesso Belmeloro located in via B. Andreatta 8, Bologna (see Fig. 1). The registration desk, **coffee breaks** and **sponsor exhibitions** will be located on the ground floor while the sessions will be held in rooms B, C and D on the first floor.

Registration desk

The **registration desk** is located in the teaching building and will be open on:

- Sunday, 1 September from 16:30 until 19:30
  (food and drinks will be served for an informal **get together**);
- Monday, 2 September from 8:15 to 12:30;
- Throughout the conference during the breaks.

Figure 1: Bologna city center and Residence.

University Residence

The **RESIDENZA ER.GO** is located in via del Carpentiere 58-60, Bologna. From the residence, the conference site can be reached by approximately 20 min bus trip. Walk to the bus stop **Carpentiere** and take bus no. **14** (runs every 15 min). Get off at the bus stop **Porta San Vitale**.

Cross the boulevard and take to your right: in approximately 50 m you will reach via Andreatta. Take via Andreatta: the conference hall is on your right (see Fig. 2).

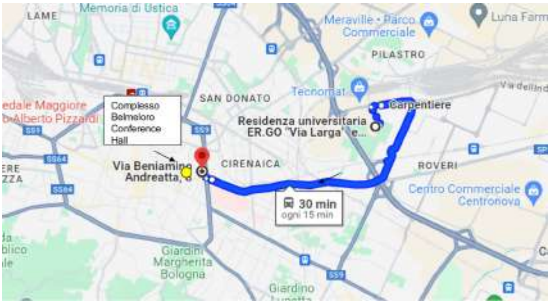

Figure 2: Way from the Residence to the Conference hall.

Meals

A **light breakfast** will be offered at the conference site starting from 8:15. For **lunch** the Mensa Universitaria, Piazza Puntoni 1, is located 400 m from the conference hall. For **supper** the mensa at Ex Scuderie dei Bentivoglio, Piazza Giuseppe Verdi 2, is open (see Fig. 3). The center of Bologna is crowded with small restaurants and bars where small meals are also served.

Figure 3: Conference sites.

Social program

The Sunday afternoon/evening **get together**, the **social dinner** and the **chamber concert** on Wednesday are included in the registration fee for both the participants and accompanying persons. The concert will be performed in the **Basilica of San Petronio** in Piazza Maggiore at 18:45.

Since the public will be allowed to enter only from 18:30 (main entrance), we ask you to arrive exactly on time or even a bit earlier to allow everybody to be seated before 18:45. After the concert, the conference dinner[1] at **Circolo Ufficiali** in Palazzo Grassi via Marsala 12 will take place. The dinner starts at 20:00 with an informal "aperitivo" buffet to allow the participants to the concert to walk from the main square to the dinner site (about 8 min, see Fig. 4). *Please, do not forget to bring your tickets to the concert and dinner; they will be required to participate in the events.*

Figure 4: University district, conference & social events sites.

Excursion

On Thursday, an **excursion** (on foot) to the Sanctuary of San Luca (on top of the "Colle della Guardia", 280 m asl), one of the symbols of Bologna, is organized. At 17:30, from Porta Saragozza, the walk under the world's longest *portico* (666 arcades) starts. After ~ 1.6 km (in about 25 min), along via Saragozza, the Meloncello Arch is reached. From there, the climbing up to the sanctuary begins (~ 1.9 km, in about 40–45 min). This second part of the walk is quite steep (498 steps) but accessible to everyone (see Fig. 5).

Figure 5: Excursion to San Luca.

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[1] Vegetarian and vegan choices will be present but catering does not guarantee the absence of cross-contamination for potential allergies such as gluten, shellfish, and nuts.

Detailed Timetable

Session MA — plenary — Monday 2/9, 9:00 – 10:30

Room B, chair: C. Puzzarini

MA.1 — **Missing ions in space and laboratory**
O. Asvany, P. C. Schmid, S. Thorwirth, S. Schlemmer
(*9:00–9:45*)

MA.2 — **Hunting interstellar molecules using rotationally-resolved laboratory spectroscopy**
M.-A. Martin-Drumel
(*9:45–10:30*)

Session MB1 — Monday 2/9, 11:00 – 12:30

Astronomy and atmospheres

Room B, chair: M. Biczysko

MB1.1 — **Millimeter-wave spectroscopy of furoic acids**
S. Chawananon, M.-A. Martin-Drumel
(*11:00–11:15*)

MB1.2 — **Microwave spectroscopy and interstellar search of *n*-propanethiol and *iso*-propanethiol**
W. Song, A. Maris, L. Evangelisti, S. Melandri, V. M. Rivilla
(*11:15–11:30*)

MB1.3 — **Characterization of cyclobutanimine via computational chemistry and microwave spectroscopy**
L. Hrubčík, T. Uhlíková, L. Kolesniková, J. Koucký, P. Kania, Š. Urban, J.-C. Guillemin
(*11:30–11:45*)

MB1.4 — **Quantum chemical and microwave spectroscopic analysis of 1-chloropropene**
T. A. Nguyen, I. Kleiner, H. V. L. Nguyen
(*11:45–12:00*)

MB1.5 — **(Sub)millimeter-wave spectroscopy of naphthalene derivatives**
M. R. Bentley, C. Rossi, U. Jacovella, M.-A. Martin-Drumel, O. Pirali
(*12:00–12:15*)

MB1.6 — **Microwave spectrum of hydantoin in its vibrational excited states**
T. Kameyama, H. Ozeki, K. Kobayashi
(*12:15–12:30*)

Session MC1 — Monday 2/9, 11:00 – 12:30

Structure determination: molecular complexes

Room C, chair: D. A. Obenchain

MC1.1 — **Room temperature detection of the dimer in the absorption spectrum of H_2**
H. Fleurbaey, S. Kassi, A. Campargue
(*11:00-11:15*)

MC1.2 — **High resolution spectrum of D_2O-CO_2 van der Waals complex around the 3OD vibrational excitation**
A. S. Bogomolov, R. Glorieux, M. Herman, N. Moazzen-Ahmadi, C. Lauzin
(*11:15-11:30*)

MC1.3 — **Rotational insights into aggregations of carbon dioxide**
Q. Gou, J. Lan, C. Wang, X. Tian, M. Li, X. Wang, J.-U. Grabow
(*11:30-11:45*)

MC1.4 — **The search for the H_2-benzonitrile complex and the friends we made along the way**
B. Hartwig, D. A. Obenchain
(*11:45-12:00*)

MC1.5 — **Conformational landscape of the complexes isopropanol$\cdots$(carbon dioxide)$_2$ using broaband chirped–pulse microwave spectroscopy**
W. Li, C. Pérez, A. Lesarri
(*12:00-12:15*)

MC1.6 — **Rotational characterization of the covalently bound dimer of acrolein: 3,4-dihydro-2H-pyran-2-carboxaldehyde ($C_8H_8O_2$).**
S. Herbers, H. V. L. Nguyen
(*12:15-12:30*)

Session MD1 — Monday 2/9, 11:00 – 12:15

Fundamental physics

Room D, chair: J.-U. Grabow

MD1.1 — **Observation of predissociative Rydberg states in a high-density molecular plasma**
F. Michels, K. Müller-Dethlefs
(*11:00-11:15*)

MD1.2 — **Investigation of the $\nu_2 = 1$, rotation-inversion $2_{1,s} \leftarrow 1_{1,a}$ transition of ammonia trough IR–millimeter-wave double resonance**
L. Juppet, O. Pirali, Y. Liu, M. Manceau, B. Darquié, O. Lopez, J. F. Lampin
(*11:15-11:30*)

MD1.3 — **Cavity-enhanced spectroscopy of H_2 in a deep cryogenic regime**
K. Stankiewicz, M. Makowski, M. Słowiński, K. L. Sołtys, B. Bednarski, H. Jóźwiak, N. Stolarczyk, S. Wójtewicz, A. Cygan, G. Kowzan, P. Masłowski, M. Piwiński, D. Lisak, P. Wcisło
(*11:30-11:45*)

MD1.4 — **Probing breakdowns of the impact approximation by cavity ring-down spectroscopy: core line intensity depletion and far-wing absorption**
Z. D. Reed, J. T. Hodges, H. Tran, J.-M. Hartmann
(*11:45-12:00*)

MD1.5 — **Vibration-rotation linelists and effective Hamiltonians from high-order canonical van Vleck operator perturbation theory**
S. V. Krasnoshchekov, I. M. Efremov, E. O. Dobrolyubov
(*12:00-12:15*)

Session MB2 — Monday 2/9, 14:00 – 16:00

Astronomy and atmospheres

Room B, chair: L. Bizzocchi

MB2.1 — **Microwave and far-infrared spectroscopy of novel species produced via high-voltage electric discharge**
J. van Wijngaarden
(keynote talk: *14:00-14:30*)

MB2.2 — **Rotational action spectroscopy of bare HCN^+ and $HCNH^+$**
W. G. D. P. Silva, O. Asvany, P. C. Schmid, L. Bonah, D. Gupta, S. Thorwirth, S. Schlemmer
(*14:30-14:45*)

MB2.3 — **Unveil the spectroscopy of the CH_3OCH_2 radical at millimeter wavelengths using Faraday rotation acquisition method**
R. Chahbazian, O. Pirali
(*14:45-15:00*)

MB2.4 — **High resolution rotational and rovibrational spectroscopy of H_2CCl^+**
O. Asvany, W. G. D. P. Silva, M. Fatima, P. C. Schmid, S. Schlemmer, S. Thorwirth, J. L. Doménech
(*15:00-15:15*)

MB2.5 — **^{13}C-isotopologues of HC_3N: characterization of the first resonance system for the three monosubstituted isotopomers**
G. Panizzi, L. Bizzocchi, M. Melosso, S. Alessandrini, C. Puzzarini, M. Nonne
(*15:15-15:30*)

MB2.6 — **Rotational spectroscopy of deuterated species: bis deuterated glycolaldehyde and *Z*-1,2-ethenediol**
M. Nonne, M. Melosso, F. Tonolo, L. Bizzocchi, S. Alessandrini, L. Dore, C. Puzzarini, J.-C. Guillemin
(*15:30-15:45*)

MB2.7 — **High resolution laboratory spectroscopy of deuterated complex organic molecules (COMs)**
H. A. Bunn, S. Spezzano, C. Endres, V. Lattanzi, L. Coudert, J.-C. Guillemin
(*15:45-16:00*)

Session MC2 — Monday 2/9, 14:00 – 15:45

Structure determination

Room C, chair: A. Maris

MC2.1 — **Influence of the binding partner on multi-conformational species: clusters analysed by rotational spectroscopy**
M. E. Sanz, V. Tsoi, S. I. Murugachandran
(keynote talk: *14:00-14:30*)

MC2.2 — **Investigation of the microsolvation of secondary organic aerosol precusors: microwave spectroscopy of nitromethoxyphenols hydrates**
C. Bracquart, A. Deguine, M. Chrayteh, A. Cuisset, J. A. Claus, M. Goubet
(*14:30-14:45*)

MC2.3 — **Conformatonal preferences of gas-phase Gly-Gly-Gly and Ala-Ala-Ala peptides investigated with VUV-IRMPD spectroscopy and quantum chemical calculations**
V. Zhaunerchyk, A. Brandt, Å. Andersson, P. Ferrari
(*14:45-15:00*)

MC2.4 — **Structural determination of dibenzothiophene and its water complex using broadband rotational spectroscopy**
F. S. Hussain, A. L. Steber, C. Pérez
(*15:00-15:15*)

MC2.5 — **Conformations of monochloropropionic acids in gas phase and solution**
F. Sun, A. Maris, L. Evangelisti, S. Melandri, C. Calabrese, A. Lesarri
(*15:15-15:30*)

MC2.6 — **The analysis of coupled torsional and inversion motions in weakly bounded ammonia-water complex**
R. A. Motiyenko, P. Gyawali, L. Margulès, E. A. Alekseev, L. Zou, I. Kleiner
(*15:30-15:45*)

Session MD2 — Monday 2/9, 14:00 – 16:00

Biology, natural substances

Room D, chair: Q. Gou

MD2.1 — **Simulation of vibrational signatures from the mid infrared (MIR) to the vacuum ultraviolet (VUV) range**
M. Biczysko
(keynote talk: *14:00-14:30*)

MD2.2 — **Formation and characterization of xanthine complexes via supersonic expansion and laser spectroscopy: a comparative study with crystal sections**
I. Usabiaga, P. Pinillos, A. Camiruaga, F. Torres, J. A. Fernández
(*14:30-14:45*)

MD2.3 — **Exploring DNA derivatives hydration: IR spectroscopy studies on water interactions with theobromine and theophylline**
P. Pinillos, A. Camiruaga, J. A. Fernández, I. Usabiaga
(*14:45-15:00*)

MD2.4 — **The influence of curcumin on tau protein aggregation**
M. Urbańska, M. Czaja, E. Lipiec, K. Sofińska
(*15:00-15:15*)

MD2.5 — **Unveiling 2-aminopyrimidine: insights from rotational spectroscopy from monomer to complexes, from millimeter to centimeter wavelengths**
C. Calabrese, M. C. Bermúdez, J. Fernández Sancho, A. Lesarri, E. M. Neeman
(*15:15-15:30*)

MD2.6 — **The enantioselective interactions of the carvone-1-phenylethanol complex**
S. I. Murugachandran, M. E. Sanz
(*15:30-15:45*)

MD2.7 — **Interactions of a conformationally rich terpenoid with water: the carvone-$(H_2O)_{1-4}$ complex**
S. I. Murugachandran, M. E. Sanz
(*15:45-16:00*)

Session MB3 — Monday 2/9, 16:30 – 18:15

Astronomy and atmospheres

Room B, chair: A. Campargue

MB3.1 — **High resolution study of the ν_{22} band of pyrrole (C_4H_5N) near 14 μm**
C. Silva Tafur, J. Vander Auwera
(*16:30-16:45*)

MB3.2 — **Towards mid-IR quantum state-resolved spectroscopy of large molecules for astrochemistry**
D. Charczun, N. Baradaran, T. Nambiar, M. L. Weichman
(*16:45-17:00*)

MB3.3 — **The $^{15}NH_3$ ammonia spectrum between 4000 and 6350 cm^{-1}.**
P. Cacciani, P. Čermák, J. Vander Auwera, A. Campargue
(*17:00-17:15*)

MB3.4 — **Extended calculations of nitrogen-induced line-broadening coefficients in the ν_7 band of ethylene**
S. Clavier, J. Buldyreva
(*17:15-17:30*)

MB3.5 — **Assignments of methyl chloride CH–stretch overtone spectra using cross–correlation pattern recognition procedure**
O. Votava, J. Rakovský, V. Svoboda
(*17:30-17:45*)

MB3.6 — **CRDS line-shape study of carbon monoxide (7–0) band**
S. Wójtewicz, A. A. Balashov, K. Bielska, J. Domysławska, R. Ciuryło, D. Lisak, G. Li, A. A. Kyuberis, N. F. Zobov, J. Tennyson, O. L. Polyansky
(*17:45-18:00*)

MB3.7 — **The O_2- and subsequently N_2-disrupted self-expansion coefficients of the ν_2, ν_5 and $\nu_3 + \nu_6$ bands of CH_3I**
S. Harbaoui, O. Fathallah, N. Maaroufi, L. Manceron, H. Aroui
(*17:45-18:15*)

Session MC3 — Monday 2/9, 16:30 – 18:15

Structure determination: molecules

Room C, chair: I. Kleiner

MC3.1 — **Low and lower: the torsional barriers of the coupled methyl internal rotations in lutidines studied by microwave spectroscopy**
M. G. Barth, S. Herbers, I. Kleiner, J.-U. Grabow, H. V. L. Nguyen
(*16:30-16:45*)

MC3.2 — **Complex hyperfine-fine structure overlapping observed in the microwave spectrum of 3,4-lutidine**
E. Antonelli, H. V. L. Nguyen
(*16:45-17:00*)

MC3.3 — **Exploring biaryl dithiolthiones using jet-cooled chirped-pulse microwave spectroscopy**
D. Heras, W. Li, M. Juanes, C. Pérez, A. Lesarri
(*17:00-17:15*)

MC3.4 — **The rotational spectra of 3-fluorobenzylamine: conformational analysis and tunnelling effects**
A. Maggio, W. Song, A. Maris, L. Evangelisti, S. Melandri, P. Pinillos
(*17:15-17:30*)

MC3.5 — **Internal rotation and structure of fluoro-substituted methyl benzoates: methyl-2-fluorobenzoate, methyl-3-fluorobenzoate, and methyl-4-fluorobenzoate**
X. Wang, P. Buschmann
(*17:30-17:45*)

MC3.6 — **Two coupled low-barrier large amplitude motions in 3,5-dimethylanisole studied by microwave spectroscopy**
S. Khemissi, L. Ferres, H. V. L. Nguyen
(*17:45-18:00*)

MC3.7 — **Investigation and characterization of oxyamines: the rotational spectrum of diethylacetyloxyamine**
F. Baroncelli, S. Melandri, L. Evangelisti, A. Maris, S. Blanco, J. C. López
(*18:00-18:15*)

Session MD3 — Monday 2/9, 16:30 – 18:00

Atmospheres

Room D, chair: P. Wcisło

MD3.1 — **Calculations of collision-induced line-shape parameters for N_2-perturbed lines in HF**
J. Behrendt, H. Jóźwiak, P. Wcisło
(*16:30-16:45*)

MD3.2 — **Ab initio quantum scattering calculations for rotational lines in HCl perturbed by O_2**
A. Olejnik, H. Jóźwiak, M. Gancewski, P. Wcisło, R. Dawes, E. Quintas-Sánchez
(*16:45-17:00*)

MD3.3 — **High temperature measurements of polarizability transition moments of CO_2**
C. Álvarez, G. Tejeda. J. M. Fernández
(*17:00-17:15*)

MD3.4 — **Databases of pressure-induced linewidths for infrared absorption by exomolecules**
J. Buldyreva
(*17:15-17:30*)

MD3.5 — **Heterodyne dispersive cavity ring-down spectroscopy for high-fidelity measurements**
A. Cygan, S. Wójtewicz, H. Jóźwiak, G. Kowzan, N. Stolarczyk, K. Bielska, P. Wcisło, R. Ciuryło, D. Lisak
(*17:30-17:45*)

MD3.6 — **Physically grounded modeling of the atmospheric gases continuum absorption in subthz range.**
E. A. Serov, T. A. Galanina, A. O. Koroleva, D. S. Makarov, I. S. Amerkhanov, M. Yu. Tretyakov
(*17:45-18:00*)

Session TB1 — Tuesday 3/9, 9:00 – 10:15

Astronomy and atmospheres

Room B, chair: K. Kobayashi

TB1.1 — **New high resolution microwave and infrared spectra for atmospheric species with large amplitude motions: the case of isoprene**
I. Kleiner, S. Khemissi, S. Herbers, H. V. L. Nguyen, I. Gulaczyk, S. Chawananon, P. Asselin
(keynote talk: *9:00-9:30*)

TB1.2 — **Coupled methyl internal rotations with intermediate and low torsional barriers in 2,5-dimethylanisole investigated by microwave spectroscopy**
H. Sun, I. Kleiner, L. Ferres, H. V. L. Nguyen
(*9:30-9:45*)

TB1.3 — **Theoretical structural and spectroscopic characterization of peroxyacetic acid ($CH_3-CO-OOH$) and dimethyl peroxide ($CH_3-OO-CH_3$): study of the far infrared region**
M. L. Senent, S. Brahem, D. Missauoia, O. Yazidi, F. Najar
(*9:45-10:00*)

TB1.4 — **Extending the rotational spectrum of cyclopentadiene towards higher frequencies and vibrational states**
L. Bonah, B. Helmstaedter, J.-C. Guillemin, S. Thorwirth, S. Schlemmer
(*10:00-10:15*)

Session TC1 — Tuesday 3/9, 9:00 – 10:30

Combustion, catalysis, kinetics

Room C, chair: T. D. Varberg

TC1.1 — **Broadband microwave spectra of reactive intermediates**
B. A. Welsh, T. S. Zwier
(keynote talk: *9:00-9:30*)

TC1.2 — **Time resolved measurements of atomic and molecular deuterium densities in a pulsed MW discharge using VUV absorption spectroscopy**
N. De Oliveira, F. J. Iguaz Gutierrez, L. Nahon, S. Bechu, M. Mitrou, P. Svarnas
(*9:30-9:45*)

TC1.3 — **Ultraviolet intracavity laser absorption spectroscopy**
U. Zamir, M. Cohen, I. Rozenberg, A. Lerer, Y. Kalisky, A. Kaplan, I. Rahinov, J. H. Baraban
(*9:45-10:00*)

TC1.4 — **Monitoring of the synthesis and temporal evolution of tritiated methane mixtures by Raman spectroscopy**
D. Diaz Barrero, T. L. Le, M. Schlösser, H. H. Telle
(*10:00-10:15*)

TC1.5 — **Aqueous-phase photoemission for chemical analysis**
L. Tomaník, P. Slavíček, B. Winter
(*10:15-10:30*)

Session TD1 — Tuesday 3/9, 9:00 – 10:30

Laser spectroscopy

Room D, chair: O. Asvany

TD1.1 — **Mass-correlated, high-resolution rotational Raman spectra**
T. Schultz, B. R. Özer, I. Heo, J. C. Lee
(keynote talk: *9:00-9:30*)

TD1.2 — **Development of 14-pole RF ion trap equipped with electrospray ion source high resolution time of flight mass spectrometer**
M. Selvaraj, U. Kadhane
(*9:30-9:45*)

TD1.3 — **The double minimum $E\,^1\Sigma_u^+$ state in $\mathbf{CS_2}$**
W. Jastrzebski, J. Szczepkowski, P. Kowalczyk, A. Pashov
(*9:45-10:00*)

TD1.4 — **IR-UV double resonance spectroscopy of formaldehyde. Part I: revealing new vibronic levels of the $\tilde{A}\,^1A_2$ state**
N. Genossar-Dan, M. Cohen, E. Brudner, J. H. Baraban
(*10:00-10:15*)

TD1.5 — **IR–UV double resonance spectroscopy of formaldehyde. Part II: the effect of vibronic coupling on cross anharmonicities**
N. Genossar-Dan, M. Cohen, E. Brudner, J. H. Baraban
(*10:15-10:30*)

Session TB2 — Tuesday 3/9, 11:00 – 12:30

Astronomy and atmospheres

Room B, chair: M. Melosso

TB2.1 — **Insigths from numerically exact approaches for the calculation of the rovibrational energy structure of tri- and tetratomic molecules**
M. Mladenović
(*11:00-11:15*)

TB2.2 — **The semi-experimental equilibrium structures of small radicals and an extension to larger species**
S. Alessandrini, M. Melosso, L. Bizzocchi, C. Puzzarini, V. Barone
(*11:15-11:30*)

TB2.3 — **An *ab initio* spectroscopic model of the carbon monoxide molecule**
M. Khalil, N. El-Kork, R. P. Brady, S. N. Yurchenko, J. Tennyson, S. J. Evans
(*11:30-11:45*)

TB2.4 — **Towards a strict diabatic representation for coupled *N*-state diatomic systems: total rovibronic equivalence**
R. P. Brady, S. N. Yurchenko
(*11:45-12:00*)

TB2.5 — **VUV and UV-Vis FT-spectroscopy of CO: analysis of the unimolecular interactions**
R. Hakalla, S. Ryzner, A. Stasik, W. Szajna, R. W. Field, N. De Oliveira, M. I. Malicka, W. Ubachs
(*12:00-12:15*)

TB2.6 — **Accessing all vibrationally excited states of the $X^{+}\,{}^{2}\Sigma_{u}^{+}$ ground electronic state of He_2^+ through multi-step laser excitation**
M. Holdener, H. Schmutz, J. A. Agner, M. Beyer, F. Merkt
(*12:15-12:30*)

Session TC2 — Tuesday 3/9, 11:00 – 12:30

Instrumental technique demonstration

Room C, chair: C. Pérez

TC2.1 — **A high-performance tunable THz source for spectroscopy and more**
S. Kassi, L. Lechevallier, L. Djevahirdjian, O. Pirali, M.-A. Martin-Drumel, R. Kassi, G. Ducournau
(*11:00-11:15*)

TC2.2 — **Raman thermometry of confined gas micro-flows**
G. Tejeda, S. Bajic, C. Álvarez, J. M. Fernández
(*11:15-11:30*)

TC2.3 — **Benchmarking a reduced-footprint broadband microwave spectrometer for simplified structure characterization**
A. Byars, S. Shipman, R. Sonstrom, J. Neill
(*11:30-11:45*)

TC2.4 — **Towards electronic spectroscopy of mass and shape selected cationic metal carbides in the context of diffuse interstellar bands**
C. Rossi, B. Gans, U. Jacovella, Y. Žabka, J. Jašík
(*11:45-12:00*)

TC2.5 — **Chirped pulse and resonator in one spectrometer (PARIS): a supersonic-jet chirp and tone fourier transform microwave spectrometer for broad acquisition and high resolution.**
H. V. L. Nguyen, S. Herbers, S. Khemissi, M. Schwell, I. Kleiner, X. Landsheere, J.-U. Grabow
(*12:00-12:15*)

TC2.6 — **Using new DC-discharge sources to investigate the formation of benzonitrile**
A. L. Steber, C. Pérez, J. R. Morán, F. Sajeev Hussain, I. Peña, A. Lesarri
(*12:15-12:30*)

Session TD2 — Tuesday 3/9, 11:00 – 12:30

Linelists and datasets

Room C, chair: F. Tamassia

TD2.1 — **pyckett and llwp – new tools to increase the efficiency of spfit/spcat**
L. Bonah, S. Schlemmer
(*11:00-11:15*)

TD2.2 — **Revisiting the $0-0$ and $1-0$ bands of the $A-X$ system of CrH with pgopher**
A. J. Ross, P. Crozet, A. Genoud, J. Morville
(*11:15-11:30*)

TD2.3 — **ExoMolHR: a relational database of empirical high-resolution molecular spectra**
J. Zhang, J. Tennyson, S. N. Yurchenko, C. Hill
(*11:30-11:45*)

TD2.4 — **Assignment of measured spectra with the marvelous methane line list**
K. Kefala, A. Owens, S. N. Yurchenko, J. Tennyson
(*11:45-12:00*)

TD2.5 — **Spectroscopic constants from rovibrational configuration interaction calculations**
D. F. Dinu, K. R. Liedl, B. Schröder, M. Tschöpe, G. Rauhut
(*12:00-12:15*)

TD2.6 — **Measurements and modeling of line parameters for the ν_3, $\nu_3+\nu_6-\nu_6$ and $2\nu_3-\nu_3$ bands of methyl fluoride at 10 μm**
M. V. Khan, M. Guinet, D. Jacquemart
(*12:15-12:30*)

Session TA — plenary — Tuesday 3/9, 14:00 – 15:30

Room B, chair: J. Tennyson

TA.1 — **Ultrafast X-ray scattering: photochemical dynamics and beyond**
A. Kirrander
(*14:00–14:45*)

TA.2 — **Testing the quantum theory with accurate laser spectroscopy**
P. Wcisło
(*14:45–15:30*)

Poster 1 — Tuesday 3 September 16:00 – 17:30

P1.01 — **UV-spectrum and photo-decomposition of peroxynitrous acid in the troposphere**
W. Chebbi, N. Derbel, A. Alijah, T. Cours

P1.02 — **Millimeter wave spectroscopy of propenethial**
K. Vávra, L. Kolesniková, J. Koucký, G. Vylitová, P. Kania, Š. Urban

P1.03 — **Going to higher J values: new measurements and assignments in the $v_t = 0, 1$ torsional states of $^{13}CH_3OH$ and $CH_3^{18}OH$**
V. Ilyushin, E. Alekseev, M. Pogrebnyak, O. Dorovskaya, H. S. P. Müller, F. Lewen, S. Schlemmer

P1.04 — **Receiving system for emission spectroscopy using a matched input filter/diplexer**
E. A. Alekseev, R. A. Motiyenko, L. Margulès, V. V. Budnikov

P1.05 — **Infrared absorption cross sections for isoprene in support of the exploration of planetary atmospheres**
K. Leroux, A. Rizopoulos, J. Vander Auwera

P1.06 — **A microwave study of the oxygenated polycyclic aromatic hydrocarbon xanthene and its hydrated clusters**
D. Loru, W. Sun, A. L. Steber, P. Ferrari, H. Nootebos, M. Schnell

P1.07 — **First analysis of the $0 - \nu''$ progression of the comet-tail system in $^{12}C^{17}O^+$**
I. Piotrowska, R. Hakalla, W. Szajna, A. Stasik, S. Ryzner, A. Para, P. Kolek, R. Kępa

P1.08 — **Terahertz measurement of rotational-inversion transitions of ammonia isotopologues**
F. Horák, Š. Urban, L. Kolesniková

P1.09 — **Gas-phase conformational landscape and structure of 1-aminoindan**
E. M. Neeman, A. Lesarri, C. Bermúdez

P1.10 — **Line-shape parameter study of methane by a mid-infrared dual-comb spectrometer**
J. Clément, O. Browet, B. Vispoel, M. Lepère

P1.11 — **High precision measurements and CRBM calculations of line shape parameters for the H_2O–N_2 collision system**
B. Vispoel, R. R. Gamache, N. G. Orphanos, K. Sung, G. C. Toon

P1.12 — **H_2O broadened by CO_2 lineshape parameters measurements for CO_2-rich atmospheres**
É. Ducreux, L. Régalia, B. Grouiez, S. Robert, M. Lepère, B. Vispoel, R. R. Gamache

P1.13 — **Line shape parameters for the H_2O–He collision system for astrophysical studies**
B. Vispoel, R. R. Gamache, N. G. Orphanos

P1.14 — **CO_2-collisional spectroscopic parameters of acetylene lines by quantum cascade laser spectroscopy**
N. Dricot, B. Vispoel, M. Lepère

P1.15 — **Determination of $CH_4 - N_2$ intermolecular potential using modified complex Robert–Bonamy formalism — preliminary work**
L. Denis, M. Lepère, B. Vispoel

P1.16 — **Line shape parameter prediction algorithm for the CO_2–H_2O collision system**
B. Vispoel, R. R. Gamache, N. G. Orphanos

P1.17 — **Generation of line-broadening parameters for molecules in the atmospheres of hot super-earths and lava planets**
A. Sokolov, S. N. Yurchenko, J. Tennyson, R. R. Gamache, B. Vispoel

P1.18 — **The ExoMol database: developments and the 2024 data release**
J. Zhang, J. Tennyson, S. N. Yurchenko, and the ExoMol Team

P1.19 — **Extension of the assignment of methyl formate in the low-lying vibrational excited state**
K. Kobayashi, M. Fujitakei, D. W. Tokaryk, B. E. Billinghurst, N. Ohashi

P1.20 — **A heterogeneous DAC/ADC-board for chirped-pulse Fourier transform spectroscopy**
P. Misra, B. Heyne, G. Grutzeck, T. Gaßen, M. Fatima, B. Klein, S. Schlemmer

P1.21 — **Absolute transition frequencies of $^{12}C_2H_2$ in the near infrared and an improved spectroscopic network at the kHz accuracy level**
V. D'Agostino, M. A. Khan, E. Fasci, S. Gravina, A. Castrillo, L. Gianfrani, T. Furtenbacher, A. G. Császár

P1.22 — **The Raman spectrum of diacetyl revisited**
M. De Lucas, F. Gámez, G. Tejeda, C. Álvarez, J. M. Fernández

P1.23 — **NO_2 reference mixtures for PEMS calibration. How much an infared spectrum can tell?**
M. E. Kim, K. Berezkin, J. Saturno, G. Li, A. Domanskaya

P1.24 — **PriSpecTemp project in progress: new measurements of *A*-band of oxygen in pure gas and mixtures with nitrogen**
K. Berezkin, A. Domanskaya, R. Stosch, G. Li

P1.25 — **Inversion splitting of the ground and some exited vibrational states of the GeH_3 radical**
G. Pitsevich, A. Malevich

P1.26 — **The experimental NH_3 line-list in the 6000-8000 cm^{-1} range.**
P. Čermák, P. Cacciani, J. Vander Auwera, O. Votava, A. Campargue

P1.27 — **The electronic spectrum of gas-phase niobium hydride, NbH**
T. D. Varberg, Z. T. P. Fried, S. Singh

P1.28 — **Spectral similarities for molecular structural identification via rigorous analysis of a new benchmark database**
R. Rahimi, N. Saban, I. Bar

P1.29 — **Spectral analysis and density profiling of the small organic molecules in protostellar sources**
J. Koucký, L. Bizzocchi, C. Puzzarini, L. Testi

P1.30 — **Rotational spectrum of 2-aminooxazole, a key prebiotic molecule in the RNA world hypothesis**
J. Koucký, E. R. Alonso, I. León, S. Mato, L. Kolesniková, K. Luková, T. Uhlíková, P. Kania, Š. Urban

P1.31 — **Exploring the rotational spectra of cyclopentylimine: insights from high-resolution millimeter wave spectroscopy**
J. Koucký, L. Kolesniková, P. Kania, Š. Urban, J.-C. Guillemin

P1.32 — **A complete *ab initio* spectroscopic dataset of the hydrogen molecule for astrophysical studies**
N. Stolarczyk, J. Behrendt, H. Jóźwiak, M. Słowiński, P. Wcisło, R. J. Hargreaves, I. E. Gordon

P1.33 — **Semi-classical calculations of line-broadening coefficients for C_2H_4 perturbed by N_2: analysis of hypotheses and technical details**
S. Clavier, J. Buldyreva

P1.34 — **High resolution rotational and rovibrational spectroscopy of H_2CCCH^+**
O. Asvany, W. G. D. P. Silva, D. Gupta, S. Thorwirth, S. Schlemmer, J. L. Doménech

P1.35 — **Systematic studies on the leak-out spectroscopy (LOS) technique in cryogenic ion traps**
J. Böing, E. Plaar, L. Von Rötel, H. Tarakji, M. Bast, T. Salomon, S. Schlemmer

P1.36 — **High-resolution rovibrational and rotational spectroscopy of CCN^+**
E. Plaar, J. Böing, S. Thorwirth, H. Tarakji, L. Von Rötel, S. Schlemmer

P1.37 — **Rotational spectroscopy of explosive taggants: study of 2,3-dimethyl 2,3-dinitrobutane**
M. Goubet, P. Dréan, E. M. Neeman, C. Bracquart, A. Deguine, A. Roucou, F. Simon, M. Chrayteh, F. Hindle, G. Mouret, A. Cuisset, J. Mory

P1.38 — **Vibrational spectroscopy of primary aliphatic amines**
V. Zelenková, L. Juha, T. Uhlíková

P1.39 — **Ultrasensitive cavity ring-down spectroscopy at 1.39 μm**
M. A. Khan, E. Fasci, V. D'Agostino, S. Gravina, A. Castrillo, L. Gianfrani

P1.40 — **Disentangling the spectra of complex organic radicals using Faraday-rotation-based millimeter-wave instrumentation.**
R. Chahbazian, L. Juppet, O. Pirali

P1.41 — **Hydrogen bonding in paraxanthine-water complexes: an *ab initio* approach**
Tanvi, G. S. S. Saini, A. Mukhopadhyay

P1.42 — **A hybrid approach to generating diatomic line lists for high-resolution studies of exoplanets and other hot astronomical objects: updates to ExoMol MgO, TiO and VO line lists**
L. K. Mckemmish, A.-M. Syme, C. A. Bowesman, K. Kefala, A. N. Perri, S. N. Yurchenko, J. Tennyson

P1.43 — **Collisional broadening of the O_2 sub-THz rotational lines**
M. A. Koshelev, I. N. Vilkov, G. Yu. Golubyatnikov, A. Yu. Sekacheva, D. S. Makarov, M. Yu. Tretyakov

P1.44 — **Free jet millimeter wave torsion-rotation spectrum of a silicon containing molecule: dimethylsylane**
A. Maggio, W. Song, A. Maris, L. Evangelisti, S. Melandri

P1.45 — **Monitoring of the synthesis and temporal evolution of tritiated methane mixtures by Raman spectroscopy**
D. Diaz Barrero, T. L. Le, M. Schlösser, H. H. Telle

P1.46 — **Recent advances on carbon disulfide molecular clusters: discovery and characterisation of new isomers**
A. J. Barclay, A. R. W. McKellar, A. Pietropolli Charmet, N. Moazzen-Ahmadi

P1.47 — **Improved Hamiltonian model for axially symmetric C_{3v} molecules: precise ro-vibrational analysis of the ground state and the ν_2/ν_4 diad of AsH_3**
O. N. Ulenikov, E. S. Bekhtereva, O. V. Gromova, S. S. Sidko, C. Sydow, S. Bauerecker

P1.48 — **Implementation of a two-color-REMPI scheme for molecular beam studies**
V. Grigorian, J. Jakob, S. Schwetje, M.A. Kaufmann, A.A. Breier, T.F. Giesen And G.W. Fuchs

P1.49 — **Deperturbation analysis of the $A^1\Pi$ $(v = 4)$ level in CO based on the VUV and Vis-FT-spectroscopies**
S. Ryzner, A. Stasik, W. Szajna, R. Hakalla, M. I. Malicka, R. W. Field, N. De Oliveira, W. Ubachs

Session WA — plenary — Wednesday 4/9, 9:00 – 10:30

Room B, chair: A. Lesarri

WA.1 — **Quantitative analysis of isotope mixtures for applications in pharmaceutical chemistry using broadband rotational spectroscopy**
B. Pate
(*9:00–9:45*)

WA.2 — **How increased use of remote sensing technique for monitoring the health of our environment translates to additional requirements as to molecular spectroscopy databases**
M. De Mazière
(*9:45–10:30*)

Session WB1 — Wednesday 4/9, 11:00 – 12:45

Atmospheres

Room B, chair: S. Yurchenko

WB1.1 — **Oxidation product analysis of an α-pinene discharge by microwave spectroscopy**
J. R. Moran, A. L. Steber, I. Peña, C. Cabezas
(*11:00-11:15*)

WB1.2 — **N_2 and O_2-broadening coefficients of CH_3Br ro-vibrational lines in the ν_2 and ν_5 bands**
I. Mejdi, H. Aroui, D. Benabdallah, N. Maaroufi, O. Ben Fathallah, F. Kwabia Tchana
(*11:15-11:30*)

WB1.3 — **Sub-mm line shape analysis of methyl bromide (CH_3Br)**
N. Osseiran, W. Tchana Betenga, F. Kwabia Tchana, J. Vander Auwera, F. Hindle, A. Cuisset
(*11:30-11:45*)

WB1.4 — **Isotopologue extrapolation of energy levels for polyatomic molecules: rotation-vibration energies of ammonia $^{15}NH_3$**
O. A. Smola, S. N. Yurchenko, J. Tennyson
(*11:45-12:00*)

WB1.5 — **Line positions and intensities of the $\nu_3 + \nu_6$ band of methyl fluoride**
H. Ziadi, M. Rey, B. Grouiez, M. Rotger, A. V. Nikitin, H. Aroui
(*12:00-12:15*)

WB1.6 — **High-resolution spectroscopy of protonated diacetylene, $H_2C_4H^+$**
D. Gupta, M. Bast, S. J. P. Marlton, S. Thorwirth, O. Asvany, T. Salomon, P. C. Schmid, S. Schlemmer
(*12:15-12:30*)

WB1.7 — **Overtone transition $2\nu_1$ of HCO^+ and HOC^+ — origin, radiative lifetime, collisional quenching**
M. Jiménez-Redondo, P. Caselli, P. Jusko, L. Uvarova, M. Kassayová, P. Dohnal
(*12:30-12:45*)

Session WC1 — Wednesday 4/9, 11:00 – 12:45

Precision spectroscopy

Room C, chair: S. Schlemmer

WC1.1 — **Precision spectroscopy of tritiated molecules**
V. Hermann
(*11:00-11:15*)

WC1.2 — **Precision measurements and tests of fundamental physics with cold molecules**
A. Bonifacio, M. Saffre, Y. Liu, N. Cahuzac, S. Tokunaga, A. Cournol, M. Gonçalves, A. Kaladjian, E. Cantin, O. Lopez, A. Amy-Klein, M. Manceau, B. Darquie
(*11:15-11:30*)

WC1.3 — **High (sub-10 mHz) resolution molecular spectroscopy in the mid-IR to THz range using broadband dual frequency comb method**
K. Vodopyanov, D. Konnov, Y.-C. Chan, E. L. Temelkova, A. Muraviev, D. Nesbitt
(*11:30-11:45*)

WC1.4 — **Unrivaled accuracy in measuring rotational transitions of greenhouse gases: THz-CRDS of CF_4**
F. Simon, A. Cuisset, C. Elmaleh, F. Hindle, G. Mouret, M. Rey, C. Richard, V. Boudon
(*11:45-12:00*)

WC1.5 — **Symmetry aspects and tunneling splittings of the torsional energy levels of the hydroquinone molecule**
G. Pitsevich, A. Malevich
(*12:00-12:15*)

WC1.6 — **Si-referenced HCOOH vibrational spectroscopy at the 20 Hz level**
M. Leuliet, A. Mbardi, B. Argence, J.-Ph. Karr, L. Hilico
(*12:15-12:30*)

WC1.7 — **A systematic reduction of the effective hamiltonians using normal ordering of cylindrical angular moment operators**
I. M. Efremov, S. V. Krasnoshchekov, D. V. Millionshchikov
(*12:30-12:45*)

Session WD1 — Wednesday 4/9, 11:00 – 12:30

Laser spectroscopy

Room D, chair: M. Lepère

WD1.1 — **Exploring molecular orbitals and ionization dynamics in 2,3-difluoropyridine: insights from high-resolution VUV-MATI mass spectroscopy**
H. Kim, S. M. Park, C. H. Kwon
(*11:00-11:15*)

WD1.2 — **Study on the conformational preference of morpholine using IR resonant VUV-PI mass spectroscopy**
S. M. Park, C. H. Kwon
(*11:15-11:30*)

WD1.3 — **Elucidating the conformational stability of tetrahydrofuran through conformer-specific vibrational spectroscopy**
C. H. Kwon
(*11:30-11:45*)

WD1.4 — **Dual frequency comb spectroscopy in the UV region with one million spectral data points resolved**
K. Vodopyanov, A. Muraviev, D. Konnov, S. Vasilyev
(*11:45-12:00*)

WD1.5 — **Comparative investigation of the dissociative photoionization of aniline induced by VUV and UV photons**
M. Selvaraj, B. Panja, U. Kadhane, R. Richter, P. Bolognesi, L. Avaldi
(*12:00-12:15*)

WD1.6 — **Analysis of the room temperature absorption spectrum of ethylene in the 6000-8050 cm^{-1} range**
O. Ben Fathallah, A. Campargue, S. Beguier, L. Manceron, M. Rey
(*12:15-12:30*)

Session ThA — plenary — Thursday 5/9, 9:00 – 10:30

Room B, chair: O. Dopfer

ThA.1 — **Precision Rydberg spectroscopy in H, He, H_2 and He_2**
F. Merkt
(*9:00–9:45*)

ThA.2 — **Cold ion trap IR spectroscopy of ion selective molecular systems**
I. S. Ishiuchi
(*9:45–10:30*)

Poster 2 — Thursday 5 September 11:00 – 12:30

P2.01 — **Line lists for four isotopologues of ammonia, NH_2D, $^{15}NH_3$, ND_3, and ND_2H**
S. N. Yurchenko, O. Smola, C. A. Bowesman, J. Tennyson, K. Batrakov, and the ExoMol team, E. Cané, F. Tamassia

P2.02 — **Investigation of the hyperfine structure of the $A^3\Sigma^+$ state in KRb**
V. Stoyanov, A. Pashov

P2.03 — **High resolution infrared spectroscopy and analysis of the spectrum of isotopically chiral *trans-c*-2,3-di-deutero-oxirane and further isotopomers**
S. Albert, K. Keppler, C. Manca Tanner, G. Wichmann, M. Quack, Z. Chen, J. Stohner, V. Schurig, O. Trapp

P2.04 — **Highly accurate thermochemical properties of the vinoxy radical**
M. R. Bentley, J. H. Thorpe, P. R. Franke, B. Ruscic, J. F. Stanton

P2.05 — **Line strength analysis of the highly excited vibrational states of H_2S: the first decade of $H_2{}^{32}S$**
O. N. Ulenikov, E. S. Bekhtereva, O. V. Gromova, E. V. Gappel, C. Sydow, S. Bauerecker

P2.06 — **Towards a theoretical ro-vibrational line list of methanol CH_3OH**
O. A. Smola, S. N. Yurchenko, J. Tennyson

P2.07 — **Ro-vibrational analysis of high-resolution FTIR spectra of the ^{13}C-enriched mixture of isotopologues of HCFC-22 ($CHClF_2$) in the 750–850 cm^{-1} spectral region**
I. M. Efremov, E. O. Dobrolyubov, S. V. Krasnoshchekov, V. B. Laptev, S. A. Klimin, O. V. Naumenko

P2.08 — **A multi-level excitation diagram analysis method applied to TiO detected at high spectral resolution in the envelope of the variable star χ Cyg**
E. Döring, J. H. Lacy, R. S. Giles, T. K. Greathouse, T. F. Giesen, G. W. Fuchs

P2.09 — **Multi-level excitation diagram analysis of infrared high resolution observations of small astrophysical molecules around late-type stars**
G. W. Fuchs, E. Döring, J. H. Lacy, R. S. Giles, T. K. Greathouse, E. Montiel, C. Dewitt, M. Richter, T. F. Giesen

P2.10 — **Room-temperature $CH_3C^{14}N$–O_2 pressure-broadening line-shape parameters in the 180–1400 GHz range**
L. Zou, F. Rohart, L. Margules, J. Buldyreva

P2.11 — **Temperature dependence of CH_3CN–N_2 line-broadening coefficients**
A. S. Dudaryonok, N. N. Lavrentieva, J. Buldyreva

P2.12 — **Composite absorption cross sections and integrated band intensities of CHF_3 in air**
K. Berezkin, M. E. Kim, G. Li, A. Domanskaya

P2.13 — **In silico assessment of radiative efficiencies and application to halocarbons**
D. Alvarado-Jiménez, N. Tasinato

P2.14 — **The nano-lego tool for accurate equilibrium structures from DFT computations**
N. Tasinato, G. Ceselin, F. Lazzari, V. Barone

P2.15 — **Impact of water vapor continuum changes on radiative efficiencies**
D. Alvarado-Jiménez, N. Tasinato, K. P. Shine

P2.16 — **Vibrational-rotational properties and climate metrics of HCFC-132b**
D. Alvarado -Jiménez, A. Pietropolli Charmet, P. Stoppa, N. Tasinato

P2.17 — **Laboratory rotational spectroscopy of potential interstellar molecules**
G. Feng, Z. Wang, Y. Li, Y. Xu, W. Li, A. Lesarri

P2.18 — **Accessing all vibrationally excited states of the $X^{+\,2}\Sigma_u^+$ ground electronic state of He_2^+ through multi-step laser excitation**
M. Holdener, H. Schmutz, J. A. Agner, M. Beyer, F. Merkt

P2.19 — **Rotational spectroscopy of secondary organic aerosol precusors: prenol and trans-2-hexenal**
C. Bracquart, A. Cuisset, J. A. Claus, M. Goubet

P2.20 — **Conformational mapping, interactions, and fluorine impact by combined spectroscopic approaches and quantum chemical calculations**
N. Saban, R. Rahimi, I. Bar

P2.21 — **Formation of radicals and small molecules in laser-induced plasmas**
P. Kohns, G. Ankerhold

P2.22 — **A new approach to enhance the sensitivity of THz-TDS**
N. Osseiran, S. Eliet, R. Peretti, F. Hindle, A. Cuisset

P2.23 — **Non-LTE infrared spectroscopy of jet-cooled naphthalene and its dissociation products for astrochemical insights**
J. Lecomte, E. Dudás, L. Biennier, R. Georges, S. Chakraborty, G. Mulas, M. Goubet, O. Pirali, S. Kassi, P. Asselin, R. W. Boswell, C. Charles

P2.24 — **Rationalizing molecular vibration through matrix isolation infrared spectroscopy and vibrational configuration interaction computations**
D. F. Dinu, K. R. Liedl, T. Loerting, G. Rauhut, H. Grothe

P2.25 — **Spectroscopic constants from rovibrational configuration interaction calculations**
D. F. Dinu, K. R. Liedl, B. Schröder, M. Tschöpe, G. Rauhut

P2.26 — **Spin-rovibrational structure of the molecular hydrogen ion from spectroscopy of Rydberg states**
I. Doran, M. Beyer, F. Merkt

P2.27 — **The new ExoMol photodissociation database**
Q. Ni, S. N. Yurchenko, M. Pezzella, J. Tennyson

P2.28 — **High-resolution spectroscopic study of vinyl cyanide isotopologues for radio astronomy: $^{13}CH_2CHCN$ and $CH_2CH^{13}CN$**
C. P. Endres, M.-A. Martin-Drumel, O. Pirali, L. Bonah, J.-C. Guillemin, M. R. Bentley, Z. Kisiel, A. Belloche, B. M. Jones, P. Schilke, S. Schlemmer, S. Thorwirth

P2.29 — **Ab initio structure and vibration-rotation dynamics of aluminum monohydroxide**
J. Koput

P2.30 — **Infrared spectroscopic study on nuclear spin conversion of matrix-isolated hydrogen**
K. Yamakawa

P2.31 — **Investigating the rotational spectrum of ^{17}O isotopic formamide: implications for astrochemistry**
N. Chen, L. Margulès, R. Motiyenko, B. Hays, M. Goubet, J.-C. Guillemin, A. Belloche

P2.32 — **Sub-millimeterwave spectrum of $CH_2{}^{35}Cl_2$, $CH_2{}^{35}Cl^{37}Cl$, and $CH_2{}^{37}Cl_2$ in the ($\nu_4 = 1$) vibrational state up to 1.1 THz**
O. N. Ulenikov, O. V. Gromova, E. S. Bekhtereva, Yu. V. Hudiakova

P2.33 — **Rotational fingerprints of 3-amino-1-propene inthe millimeter wave spectral region**
L. Kolesniková, J. Koucký, B. N. Dangová, P. Kania, Š. Urban

P2.34 — **Utilisation of a high repetition discharge nozzle in a molecular beam setup**
S. Schwetje, J. Jakob, V. Grigorian, M. A. Kaufmann, A. A. Breier, G. W. Fuchs, T. F. Giesen

P2.35 — **Rotational-vibrational analysis of selected strong fundamentals in $PF^{35}Cl_2$ and $PF^{35}Cl^{37}Cl$**
V. Horká-Zelenková, A. Sieben, S. Albert, K. Keppler, G. Seyfang, G. Wichmann, M. Quack, J. Stohner

P2.36 — **Microwave spectrum of the three lowest torsional states of dimethylether $(CH_3)_2O$**
V. Ilyushin, E. Alekseev, Y. Bakhmat, O. Dorovskaya, B. J. Drouin, S. Schlemmer, H. S. P. Müller, C. P. Endres

P2.37 — **Extensive study of dense rotational spectra of the chiral molecule chlorofluoroacetonitrile**
K. Luková, W. Sun, K. Vávra, D. Kargin, M. Schnell, G. W. Fuchs, T. F. Giesen

P2.38 — **First results of IR–UV double resonance with the cold molecular beam apparatus**
J. Jakob, V. Grigorian, S. Schwetje, M. A. Kaufmann, G. W. Fuchs, T. F. Giesen, A. A. Breier

P2.39 — **Fluorescence and mass-selective spectroscopy of small silicon carbides: the $\tilde{C}\Sigma_u^- \leftarrow \tilde{A}\Sigma_g^-$ transition of *l*-SiCCSi**
J. Flores, D. Kaur, N. J. Reilly

P2.40 — **High-resolution spectroscopy and multichannel quantum-defect-theory analysis of high Rydberg states of rare-gas atoms**
E. N. Toutoudaki, H. Herburger, U. Hollenstein, F. Merkt

P2.41 — **Radiative and tunneling decay dynamics in the $A\,^3\Sigma_u^+ - C\,^3\Sigma_g^+$ system of He_2**
F. Wirth, M. Holdener, M. Beyer, F. Merkt

P2.42 — **Collisional parameters of $R(0)$ transition of CO in N_2**
D. S. Makarov, E. A. Serov, I. N. Vilkov, T. A. Galanina, A. O. Koroleva, M. A. Koshelev, M. Yu. Tretyakov

P2.43 — **Chirality in tetraethyllead induced from an achiral structure through non-covalent interactions**
W. Sun, M. Schnell

P2.44 — **Investigation on THz solid state sources — evaluation for spectroscopic use**
M. V. Khan, M. Guinet, P. Soulard, H. Elandaloussi, F. Hindle

P2.45 — **A true Omega representation as an adiabatic transformation of spin-orbit interactions and their associated non-adiabatic couplings**
R. P. Brady, S. N. Yurchenko

P2.46 — **Heterodyne-based high-resolution THz spectroscopy on the AILES beamline of SOLEIL synchrotron and precision millimeter-wave spectroscopy of radical species**
L. Juppet, M.-A. Martin-Drumel, O. Pirali, G. Mouret, F. Hindle, A. Khabbaz, J. F. Lampin

P2.47 — **Correlated rotational alignment spectroscopy and structure of benzene**
I. Heo, B. R. Özer, J. C. Lee, W. Sarquah, T. Schultz

P2.48 — **Correlating parent-fragment relationships in CS_2 cluster photoionization**
B. R. Özer, I. Heo, J. C. Lee, T. Schultz

P2.49 — **Characterization and photochemistry of XCO_2 (X = F, NH_2, CH_3) radicals**
S. Kechoindi, S. Ben Yaghlane, N. Terzi, J. Palaudoux, M. Hochlaf

Session ThB1 — Thursday 5/9, 14:00 – 16:00

Astronomy and atmospheres

Room B, chair: G. Fuchs

ThB1.1 — **Photochemical properties of astrochemically-relevant silicon clusters: bridging the gap between diatomics and silicate grains**
O. Dopfer
(keynote talk: *14:00-14:30*)

ThB1.2 — **Temperature-dependent photodissociation cross sections and rates for H_2S**
A. N. Perri, S. N. Yurchenko, J. Tennyson, A. O. Mitrushchenkov
(*14:30-14:45*)

ThB1.3 — **Discovery of a new electronic state in iron hydride assigned to** $(2)^4\Phi$
T. Blackmore, D. Tokaryk, A. Adam, P. Crozet, A. J. Ross
(*14:45-15:00*)

ThB1.4 — **Rotationally resolved PFI-ZEKE photoelectron spectroscopy of the CH_3 radical probing the $X^+\ {}^1A_1'$ ($\nu_2{}^+ = 1$ and $\nu_4{}^+ = 1$) levels of the $CH_3{}^+$ cation**
N. Chen, H. Le, B. Gans, S. Boyé-Péronne, P. B. Changala, C. Alcaraz
(*15:00-15:15*)

ThB1.5 — **Photoelectron spectroscopy of small free radicals at medium- and high-spectral resolution**
N. Chen, H. Le, S. Boyé-Péronne, B. Gans
(*15:15-15:30*)

ThB1.6 — **Stellar wind contribution to origin and transport of water on the surface of oxygen-containing minerals, Part I**
S. Civiš, J. Kubišta, J. Plšek, A. Knížek
(*15:30-15:45*)

ThB1.7 — **Stellar wind contribution to origin and transport of water on the surface of oxygen-containing minerals, Part II**
S. Civiš, J. Kubišta, J. Plšek, A. Knížek
(*15:45-16:00*)

Session ThC1 — Thursday 5/9, 14:00 – 16:00

Non covalent interactions

Room C, chair: H. L. V. Nguyen

ThC1.1 — **Molecular beam microwave spectroscopy: large amplitude motions and non-covalent bonds**
E. Arunan
(keynote talk: *14:00-14:30*)

ThC1.2 — **Rotational spectroscopic study of the PA-FA-PHS complex**
J. Hong, W. Li, M. Zhou
(*14:30-14:45*)

ThC1.3 — **Interactions of a ketone with a higher number of waters in the gas phase: structures and binding preferences of cyclooctanone$\cdots$(H_2O)$_{3-8}$ clusters**
V. Tsoi, E. Burevschi, M. E. Sanz
(*14:45-15:00*)

ThC1.4 — **Configurations of *o*-phthalaldehyde–(H_2O)$_{1-3}$ complexes elucidated by rotational spectroscopy**
V. Tsoi, M. E. Sanz
(*15:00-15:15*)

ThC1.5 — **Rotational spectroscopy and tautomeric equilibria in complexes formation of benzisothiazolinone**
J. Li, D. Loru, W. Sun, M. Schnell
(*15:15-15:30*)

ThC1.6 — **Rotation visualizing solvation: studying oligo hydrates of 4-hydroxy-2-butanone**
M. Li, J.-U. Grabow, W. Li, C. Pérez, A. Lesarri
(*15:30-15:45*)

ThC1.7 — **Microwave spectroscopic study of solvation processes in $\pi - \pi$ stacking**
X. Chen, G. Wang, X. Zeng, W. Li, M. Zhou
(*15:45-16:00*)

Session ThD1 — Thursday 5/9, 14:00 – 16:00

Laser spectroscopy

Room D, chair: O. Pirali

ThD1.1 — **Jet-cooled mid-infrared laser spectroscopy of centrosymmetric and N-bearing PAHs**
P. Asselin, S. Chawananon, O. Pirali, M. Goubet
(keynote talk: *14:00-14:30*)

ThD1.2 — **Far infrared absorption spectroscopy of the nine stable isotopologues of water vapor**
S. N. Mikhailenko, A. O. Koroleva, E. V. Karlovets, A. Campargue
(*14:30-14:45*)

ThD1.3 — **Experimental determination of the Landé *g*-factors for the $N = 1$ rotational energy levels in the ground vibronic state ($X^3\Sigma_g^-, v = 0$) of $^{16}O_2$**
A.-W. Liu, Y.-R. Xu, Z.-T. Zhang, Y.-Q. Cheng, Y. Tan, S.-M. Hu
(*14:45-15:00*)

ThD1.4 — **Si-traceable density measurement of H_2 based on polarizability and absorption spectroscopy**
S.-M. Hu, H. Liang, Z.-L. Nie, J. Wang, Y. Tan, C.-L. Hu, C.-F. Cheng, A.-W. Liu, Y. R. Sun
(*15:00-15:15*)

ThD1.5 — **Cavity ring-down spectroscopy of jet-cooled ethylene between 5880 and 6200 cm^{-1}**
S. Perot, J. Lecomte, N. Suas-David, L. Rutkowski, R. Georges, M. Rey, S. Kassi
(*15:15-15:30*)

ThD1.6 — **High resolution dual frequency comb spectroscopy from 1 THz to 1 PHz**
K. Vodopyanov
(*15:30-15:45*)

ThD1.7 — **Spectroscopic study of a single molecule underneath the STM tip**
A. Farrukh
(*15:45-16:00*)

Session FA — plenary — Friday 6/9, 9:00 – 10:30

Room B, chair: M. E. Sanz

FA.1 — **Magnetic resonance of biomolecules by combining ESR and NMR techniques**
M. Bennati
(*9:00–9:45*)

FA.2 — **Rotational insights into sulfur-mediated non-covalent interactions**
G. Feng, L. Wang, T. Yang, W. Lv, J. Huang, H. Huang, Y. Li, F. Shen, Y. Feng
(*9:45–10:30*)

Session FB1 — Friday 6/9, 11:00 – 12:15

Astronomy and atmospheres

Room B, chair: S. Thorwirth

FB1.1 — **Searching for resonances states by complex scaling**
T. Uhlíková, S. Yurchenko
(*11:00-11:15*)

FB1.2 — **Where experiment meets theory: the way to the new ExoMol line lists–LIV for AlH and AlD**
W. Szajna, R. Hakalla, S. N. Yurchenko, J. Tennyson, M. Semenov, A. Sokolov, R. R. Gamache, Y. Pavlenko, M. R. Schmidt, R. W. Field
(*11:15-11:30*)

FB1.3 — **Towards accurate climate metrics by quantum chemical spectroscopic simulations**
D. A. Alvarado-Jiménez, N. Tasinato
(*11:30-11:45*)

FB1.4 — **Theoretical vibrational analysis and Raman spectra of acetone isotopologues**
S. Dalbouha, C. Alvarez, G. Tejeda, J. M. Fernandez, M. L. Senent
(*11:45-12:00*)

FB1.5 — **Machine learning estimate of the interstellar physical conditions from the observed spectral line profiles**
E. Mendoza, P. Dall'Olio, M. Carvajal, L. S. Coelho, A. Peregrín, S. López-Domínguez, F. F. S. Van Der Tak
(*12:00-12:15*)

Session FC1 — Friday 6/9, 11:00 – 12:30

Linelists and datasets

Room C, chair: A. Ross

FC1.1 — **Multi-laboratory comparison of $^{12}C^{16}O$ $(3-0)$ line intensities: towards primary spectroscopic measurements of amount of gas**
K. Bielska, V. D'Agostino, S. Wójtewicz, A. Cygan, R. Ciuryło, D. Lisak, J. T. Hodges, Z. D. Reed, M. Birk, G. Wagner, C. Röske, R. Guo, G. Li
(*11:00-11:15*)

FC1.2 — **Pressure and temperature dependencies of air-perturbed O_2 *B*-band line shapes**
K. Bielska, D. D. Tran, A. A. Balashov, J. Domysławska, S. Wójtewicz, M. Bober, S. Bilicki, R. Ciuryło, D. Lisak
(*11:15-11:30*)

FC1.3 — **Ab initio quantum scattering calculations for N_2-perturbed R(0) 3–0 line in CO**
A. Olejnik, H. Jóźwiak, N. Stolarczyk, M. Żółtowski, P. Wcisło, H. Cybulski, B. Fernández, C. Henriksen
(*11:30-11:45*)

FC1.4 — **N_2-collisional broadening of N_2O lines: high-resolution dual-comb spectroscopy and semi-classical line shape calculations**
B. Vispoel, R. R. Gamache, M. Lepère
(*11:45-12:00*)

FC1.5 — **Collisional excitation of PO^+ by *para*-H_2**
F. Tonolo, L. Bizzocchi, M. Melosso, C. Puzzarini, V. M. Rivilla, F. Lique
(*12:00-12:15*)

FC1.6 — **The collision-induced absorption of H_2 near 1.20 μm: subatmospheric measurements and validation tests of calculations**
A. O. Koroleva, S. Kassi, H. Fleurbaey, A. Campargue
(*12:15-12:30*)

Session FD1 — Friday 6/9, 11:00 – 12:00

Comparing theory and experiment

Room D, chair: S. Alessandrini

FD1.1 — **A full-symmetry torsion rotation theoretical approach for nitromethane CH_3NO_2**
I. Gulaczyk, M. Kreglewski
(*11:00-11:15*)

FD1.2 — **Sweetness and light: computation of the rotational spectra of proto-saccharides**
M. Sang, T. E. Field-Theodore, P. R. Taylor
(*11:15-11:30*)

FD1.3 — **Millimeter-wave spectrum of 2-hydroxyacetophenone and 2-aminoacetophenone**
S. Boi, S. Melandri, L. Evangelisti, A. Maris
(*11:30-11:45*)

FD1.4 — **Theoretical study of the CH_3Br+N_2 van der Waals complex: potential energy surface and applications**
I. Mejdi, D. Benabdallah, H. Aroui, M. Hochlaf
(*11:45-12:00*)

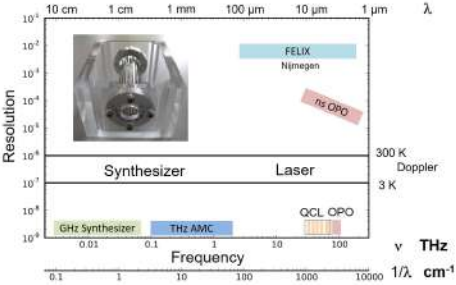
Invited Speaker MA
Monday, September 2, 9:00
Chair: C. Puzzarini
Room B

Missing ions in space and laboratory

O. Asvany[1] **,** ***P. C. Schmid***[1] **,** ***S. Thorwirth***[1] **,** ***S. Schlemmer***[1]

[1] I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, (Germany)

Action spectroscopy in cryogenic higher-order multipole ion traps as depicted in the insert of the Figure below was instrumental to overcome limitations of traditional ways of ion spectroscopy. Mass selection paired with low temperature storage and near unity ion detection efficiency are unique features of these techniques [1]. Today narrow band infrared lasers are commercially available and allow to record rotationally resolved vibrational spectra (see Fig.). In our newly developed leak-out spectroscopy (LOS) method the ions of interest are kicked-out from the trap based on a vibration-to-translation energy transfer [2]. We use the highly accurate THz radiation from amplifier multiplier chains (THz AMC, see Fig.) to employ THz-infrared double resonance schemes in order to also record pure rotational transitions [3]. Based on these spectra several ionic species have been found in space, e.g., [4]. Moreover, LOS is a spectroscopic tool to analyse the composition of an isobaric ion cloud. We use this possibility to determine the ortho to para ratio of H_3^+ and other ions but also to prepare clean isomeric samples. Therefore, new classes of experiments can be performed under the controlled trap conditions.



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Hunting interstellar molecules using rotationally-resolved laboratory spectroscopy

M.-A. Martin-Drumel[1]

[1] Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405 Orsay (France)

The identification of new molecules in the interstellar medium (ISM) is often intrinsically linked to their prior study in the laboratory, especially at high (i.e., rotationally-resolved) resolution because then the recorded spectra act as identity cards for the molecules. Yet, current astronomical surveys—recorded using instruments as the GBT, Yebes telescope, ALMA, and JWST—display a wealth of transitions that cannot be assigned to any known molecule. Laboratory data, in particular rest frequencies in the range where these instruments operate, is thus more than ever needed.

From an Earth-experimentalist point of view, the candidates for interstellar detection can be sorted into two groups: stable and reactive species. The recent interstellar detection of the first PAHs-type molecules (e.g., benzonitrile, cyanonaphthalenes, and indene), after decades of unsuccessful searches, has brought the first group of molecules back into light and stresses the need for new laboratory data on related relatively large compounds. As for the second group, although reactive species represent a significant amount of the known interstellar species (more than 50 In this talk, I will present some of the recent results on known or postulated astronomical species from our group, with emphasis on the first laboratory gas phase observation of the H_2NCO radical and the interstellar detection of the CH_3^+ cation.

Contributed speaker MB1

Monday, September 2, 11:00
Chair: M. Biczysko
Room B
Astronomy and atmospheres

Millimeter-wave spectroscopy of furoic acids

S. Chawananon[1] **, *M.-A. Martin-Drumel***[1]

[1]Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405 Orsay (France)

Furans and their derivatives, including methylfurans (c-C_4H_3O-CH_3) and furfural (c-C_4H_3O-CHO), are major volatile organic compounds (VOCs) contributing significantly to atmospheric pollution and the formation of Secondary Organic Aerosols (SOAs) [4]. Furoic acids (FAs; c-C_4H_3O-COOH), as oxidation byproducts of the aforementioned species, are influential in atmospheric chemistry, potentially altering SOA mass and composition, and promoting acid rain [5]. Microwave gas phase rotational spectroscopy has has been employed to elucidate the structure and dynamic changes of 2-furoic acid (2-FA), [6], but no equivalent high-resolution study exists for 3-FA to the best of our knowledge. Here, we report the rotational spectroscopy of the 2-FA and 3-FA isomers, focusing on their monomeric conformers. The spectra were recorded at room temperature using millimeter-wave chirped-pulse spectroscopy in the 75 to 110 GHz range, with each spectrum resulting from about 1 h of acquisition time yet achieving a S/N over 500. The spectral analysis was guided by quantum chemical calculations at the B3LYP/6-311++g(d,p) level of theory. For the two lowest energy conformers of each isomer in their vibrational ground state, assignments were straightforward using the rotational constants from [6] for 2-FA and our calculations for 3-FA. However, identifying and analyzing vibrationally excited states posed challenges due to the numerous vibrational satellites with significant intensity coupled with the minimal difference in rotational constants for the different conformers (less than 10 MHz). Nevertheless, spectroscopic assignments were achieved for the lowest vibrationally excited states (torsion of –COOH) of each species with up to 3 quanta of vibrational excitation. This research not only provides a reliable set of spectroscopic constants (rotational and quartic centrifugal distortion constants) for the studied FA compounds but also illustrates the utility of CP spectroscopy for analyzing complex organic mixtures with multiple isomers and conformers at room temperature.

References

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Microwave spectroscopy and interstellar search of *n*-propanethiol and *iso*-propanethiol

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Sulfur-bearing molecules are crucial for studying star-forming regions [1, 2] and monitoring hot core evolution [3]. This study investigates the rotational spectra of two isomers of propanethiol: *n*-propanethiol (nPT, $CH_3CH_2CH_2SH$) and *iso*-propanethiol (iPT, $(CH_3)_2CHSH$). These molecules are of particular interest in astrochemistry due to their potential roles in the complex chemical networks of the interstellar medium (ISM). Notably, analogous molecules such as propanol have been detected in the ISM toward two sources [4, 5]. These detections encourage us to measure the rotational spectra of the sulfur analogs of propanol.

The rotational spectra of nPT and iPT were recorded using a Stark-modulated free-jet millimeter-wave absorption spectrometer covering the range 59.8-78 GHz. Two conformations were characterized for each molecule. Specifically, both the *TG* conformer of nPt and the *gauche* conformer of iPT exhibit a doubling for the transitions in the recorded spectra.

Accurate spectroscopic parameters were determined and utilized to generate a line catalog that has been used to perform the interstellar search. An ultra-sensitive spectral survey of the Galactic Center molecular cloud G+0.693-0.027 was used, which is based on observations conducted with the IRAM 30m and Yebes 40m telescopes. This source is an excellent candidate to search for propanethiol because several S-bearing species have been detected towards it for the first time in space (Rodríguez-Almeida et al.[8] and Sanz-Novo et al.[9]), and propanol has also been previously detected (Jiménez-Serra et al.[4]). Despite an exhaustive search, neither nPT nor iPT was detected in this region, and we have upper limits for their abundances.

References

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Characterization of cyclobutanimine via computational chemistry and microwave spectroscopy

L. Hrubčík[1] **, *T. Uhlíková*[1] , *L. Kolesniková*[1] , *J. Koucký*[1] , *P. Kania*[1] , *Š. Urban*[1] , *J.-C. Guillemin*[2]**

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Imines, in general, have great prebiotic potential as building blocks of biologically interesting species due to their unsaturated C=N-R bond. Small imines have already been observed in interstellar matter (ISM) as well as several cyclic compounds. Cyclic molecules require specific physicochemical conditions (PCCs) for their formation. Systematic laboratory rotational studies of cyclic species are fundamental for their unambiguous interstellar identifications and explorations of PCCs in regions where they reside. In this work, the target molecule is cyclobutanimine, for which the rotational spectrum has never been investigated.

The spectral characteristics of cyclobutanimine were first studied theoretically using Coupled-Cluster via the Cfour program package. Since the lowest vibrational mode encompasses large amplitude motion of the ring, the scan of potential energy curve (PEC) along with the ring inversion coordinate was proceeded. The PEC exhibited a double minimum potential with two equivalent minima separated by a low barrier to the planar ring geometry. The associated energy level splitting was studied based on the variational Hamiltonian developed by Prof. Senent[2, 3].

On the experimental side, the room-temperature rotational spectra were measured in selected frequency regions between 204 and 326 GHz using the Prague semiconductor millimeter wave spectrometer[4]. The analysis of the spectra revealed considerable perturbations that agree with the double minimum potential predicted for cyclobutanimine. First results concerning the ground state and excited vibrational states will be presented.

References

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Quantum chemical and microwave spectroscopic analysis of 1-chloropropene

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1-chloropropene is one of the halogen derivatives of propene. It belongs to an important substance group playing a major role in astrophysics and atmospheric chemistry. 1-chloropropene exists in two isomer forms, *E* and *Z*, with respect to the orientation between the methyl group and the chlorine atom. The aim of this work is to re-examine its gas phase structures and methyl internal rotation [1, 2] using a combination of pulsed molecular jet Fourier transform microwave spectroscopy and quantum chemical calculations. Due to the methyl torsion, all rotational transitions split into an A and an E torsional species. In addition, each of the two torsional species contains further hyperfine splittings arising from the interaction of the quadrupole moment of the chlorine nucleus with the surrounding electric field gradient. The microwave spectra were measured in the frequency range from 2 to 40 GHz. Quantum chemical calculations were performed to obtain the optimized molecular geometries as well as predicted methyl torsional barriers and chlorine nuclear quadrupole coupling constants. The complex spectral splittings were analyzed and fitted to obtain experimental molecular and internal rotation parameters which validated quantum chemical results. The non-bonded intramolecular electrostatic attraction between the methyl group and the chlorine atom overcomes steric hindrance, leading to higher stability of the *Z* isomer. The consequence is a radical decrease of the methyl torsional barrier in the *Z* isomer due to steric repulsion.

References

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(Sub)millimeter-wave spectroscopy of naphthalene derivatives

M. R. Bentley[1] ***, C. Rossi***[2] ***, U. Jacovella***[2] ***, M.-A. Martin-Drumel***[2] ***, O. Pirali***[2]

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Following recent discoveries in the interstellar medium of the first cyclic and polycyclic aromatic hydrocarbons using rotational spectroscopy, namely benzonitrile (c-C_6H_5–CN) and cyanonaphthalene (c-$C_{12}H_7$–CN) [1], renewed attention is given to derivatives of aromatic molecules and large carbonaceous species. The presence of a –CN group, for instance, significantly increases the permanent dipole moment value of a carrier compared to the parent species, enhancing carrier detectability in the interstellar medium. For species whose parent molecule possesses a permanent dipole moment, it is possible to study the column density ratios between substituted and unsubstituted species; some examples include indene (c-C_9H_8 v.s. c-C_9H_7–CN)[2] and cyclopentadiene (c-C_5H_6 v.s. c-C_5H_5–CN)[3]. Other polar groups may render certain molecules detectable but laboratory data on these species is often lacking. In this context, we have undertaken laboratory spectroscopic investigations of the pure rotational spectrum of several polar naphthalene derivatives (containing a –CN, –CH_3, –SH, –NH_2, C_2H, or –C_2H_3 group) at millimeter and submil- limeter wavelengths. We employed both a chirped-pulse millimeter-wave and frequency-modulation (sub)millimeter-wave spectrometers to record room-temperature spectra from 75 to 220 GHz. Some species have already been investigated at microwave wavelengths in the literature[4]; for others we report the first laboratory observation by means of pure rotational spectroscopy. For the latter, spectroscopic assignments were guided by quantum-chemical calculations. In this talk, we report on the measurement and assignment of the different spectra.

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Microwave spectrum of hydantoin in its vibrational excited states

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The rotational spectrum of the molecule hydantoin $H_4C_3N_2O_2$, a hetero five-membered ring compound known as one of the amino acid precursors, was measured in the frequency range of 80-180 GHz. The hydantoin sample is a solid at room temperature, we obtained the vapor pressure required for the measurement by heating it to 120 degrees Celsius. Since many satellite bands were observed in addition to those being assigned to the ground state, which were already reported in the previous work [1]. These were assigned to the rotational transitions in the (at least) five low-lying vibrational excited states predicted from the first-principles calculations. In this paper, we will report our results of spetcral analysis, taking into account Coriolis interactions between the vibrational excited states.

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Contributed speaker MC1
Monday, September 2, 11:00
Chair: D. A. Obenchain
Room C

Structure determination: molecular complexes

Room temperature detection of the dimer in the absorption spectrum of H_2

H. Fleurbaey[1] **, *S. Kassi***[1] **, *A. Campargue***[1]

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The absorption spectrum of pure gas phase H_2 in standard conditions is generally seen as the sum of two contributions: sharp and weak electric quadrupole monomer lines, and a broad collision-induced absorption (CIA) continuum due to the dipole induced by molecular collisions. In recent years, we studied the first overtone (2-0) rovibrational spectrum of H_2 around 1.2 μm by cavity ring-down spectroscopy (CRDS). We have previously determined the positions and line shapes of quadrupole lines [1], as well as the CIA contribution [2]. A new CRDS broadband room-temperature investigation of the same region at high sensitivity and high resolution revealed unexpected features, some of which surrounding quadrupole monomer lines.

These very weak, partly resolved spectral features were identified as $(H_2)_2$ dimer absorption by comparison with measurements by McKellar [3] performed in the fundamental band (1-0), but at a much colder temperature of 20 K. We report here the first detection at room temperature and sub-atmosphere pressures of this very weakly bound van der Waals complex (binding energy on the order of 3 cm^{-1}, to be compared to a thermal energy $k_B T \approx 200$ cm^{-1}). Analysis of the observed features provides insight on the structure of this elusive species and its unexpected detection at room temperature.

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High resolution spectrum of D_2O-CO_2 van der Waals complex around the 3OD vibrational excitation

A. S. Bogomolov[1] ***, R. Glorieux***[1] ***, M. Herman***[2] ***, N. Moazzen-Ahmadi***[3] ***,***
C. Lauzin[4]

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Water and CO_2 are the most important greenhouse gases in our atmosphere. The solvation of CO_2 is a decisive process in the chemistry of clouds and oceans. A precise characterization of the interaction of these two molecules is thus of prime importance. In the present work, we recorded the rotationally resolved spectrum associated to the triple excitation of the OD stretch in the D_2O-CO_2 molecular complex. This represents a further step in our longstanding effort to characterize better the dynamics of the interaction of CO_2 and H_2O notably through a systematic increase of the vibrational excitation [1, 2, 3]. All the measurements were performed using the FANTASIO experimental setup [3, 1]. The complexes were formed using an 8 cm long pulsed slit supersonic jet and probed using the CRDS technique in the spectral range of the second OD overtone of D_2O, i.e. 1.27 μm. The recorded spectrum was vibrationally assigned to the $(v_1, v_2, v_3) \leftarrow (v_1', v_2', v_3') = (2,0,1) \leftarrow (0,0,0)$ where v_1, v_2, v_3 are the vibrational quantum numbers of the isolated D_2O molecule. The experimental spectrum and the improvements of the experimental setup which allowed the recording of this spectral signature will be presented. I will discuss our progress in spectrum analysis using group theory and an effective Hamiltonian.

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Rotational insights into aggregations of carbon dioxide

Q. Gou[1] ***, J. Lan***[1] ***, C. Wang***[1] ***, X. Tian***[1] ***, M. Li***[2] ***, X. Wang***[2] ***, J.-U. Grabow***[2]

[1] Departments of Chemistry, School of Chemistry and Chemical Engineering, Chongqing University, Daxuecheng South St. 55, 401331 Chongqing (China), [2] Institut für Physikalische Chemie & Elektrochemie Leibniz Universität Hannover, Callinstraße 3A, 30167 Hannover, (Germany)

Carbon dioxide, a significant greenhouse gas, is also a widely used supercritical solvent. The formation of clusters with organic molecules, and their structural and bonding patterns, are critical for the atmospheric and solvation processes. The non-covalent interactions between carbon dioxide and various substances, which drive these processes, are still poorly understood.High-resolution rotational spectroscopy, known for its molecular structure fingerprinting capabilities, offers a powerful means to investigate these bonding patterns and structural changes in clusters, both from structural and energetic perspectives. Using the precise capabilities of rotational spectroscopy, our study has systematically analyzed the bonding patterns and structural transitions from dimers [1, 2] to oligomers in clusters involving small organic molecules with carbon dioxide. Additionally, we have examined the competitive interactions between water and carbon dioxide in hetero-ternary clusters, shedding light on their complex intermolecular dynamics..

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The search for the H_2-benzonitrile complex and the friends we made along the way

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Benzonitrile is among the few benzene derivatives that have been observed in the interstellar medium [1]. Since H_2 is commonly found in outer space the complex of benzonitrile with H_2 is of special interest in an astrochemical context. The resulting dimer could serve as precursor for the hydrogenation reaction of benzonitrile, possibly mediated by grain surface interactions in space. In this way, benzylamine or even toluene could be formed in the interstellar medium [2, 3]. Calculations indicate that H_2 binds to the phenyl-ring of the benzonitrile, but in comparison to other such complexes it is tilted towards the cyano-group instead of being bound in a linear fashion which could favour the hydrogenation reaction. We aim to find the H_2-benzonitrile complex using cavity microwave jet-spectroscopy. The special spectral features that arise due to the presence of *ortho* and *para* H_2 provide an additional experimental and computational challenge. Other previously unmeasured/unassigned aggregates further complicate the spectra.

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Conformational landscape of the complexes isopropanol $\cdots$ (carbon dioxide)$_2$ using broaband chirped-pulse microwave spectroscopy

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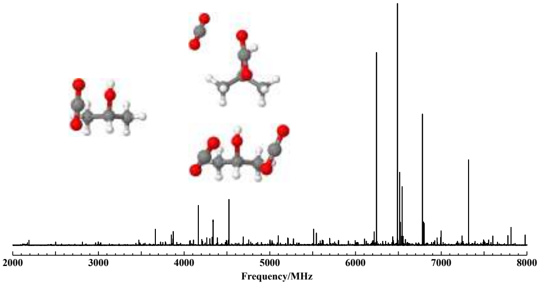
Carbon dioxide is one of the major contributors to the greenhouse effect and atmospheric dynamics. For this reason, the investigation of weakly-bound intermolecular complexes of carbon dioxide may help to understand the early stages of nucleation and formation of aerosols and clouds. Numerous studies have shown that Fourier transform microwave spectroscopy can provide effective assistance for the study of non-covalent interactions. Currently, rotational investigations on non-covalent interactions between small molecules and carbon dioxide are emerging [1-3]. Here, we investigated the non-covalent interactions between isopropanol (IPP) and carbon dioxide (CO_2) using broadband chirped-pulse excitation technology. The results have shown that isopropanol can adopt multiple conformations when interacting with carbon dioxide. Currently, we have assigned one conformer (trans-CO_2) for IPP-CO_2 with one $C\cdots O$ bond and one $CH\cdots O$ bond, and two conformers (trans-CO_2 and gauche-CO_2) for IPP-$(CO_2)_2$ with $C\cdots O$ bonds and $CH\cdots O$ bonds. More details about the experiment and theoretical calculations will be presented during the conference.



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Rotational characterization of the covalently bound dimer of acrolein: 3,4-dihydro-2H-pyran-2-carboxaldehyde ($C_8H_8O_2$)

S. Herbers[1] **, *H. V. L. Nguyen***[1]

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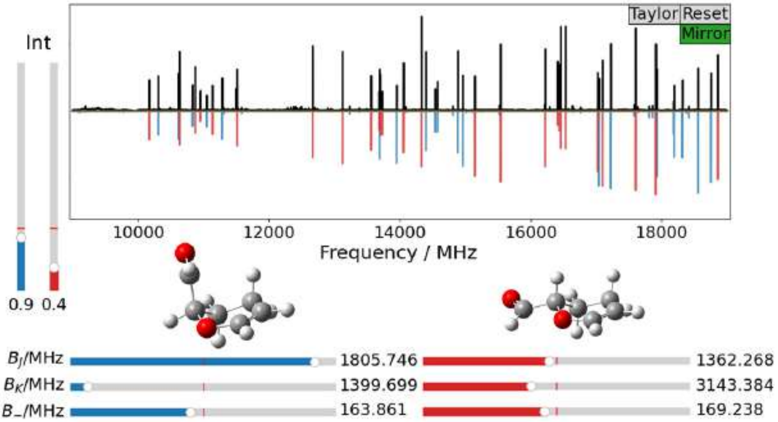
The product of acrolein dimerization (3,4-Dihydro-2H-Pyran-2-carboxaldehyde), relevant to atmospheric chemistry in context of secondary aerosol formation, was investigated using molecular jet Fourier-transform microwave spectroscopy. A new spectral assignment tool 'Analysis Program Extension for XIAM and more' (*APEX*) has been developed that allowed for swift identification of two conformers, one with axial aldehyde group (*ax*) and one with equatorial aldehyde group (*eq*). The abstract figure shows a screenshot of *APEX*'s user interface together with the structures of the two conformers. Inspired by a tool available within the *JB64* program [1], *APEX* is based on a second order Taylor expansion. The user can change rotational constants and observe the effect on the predicted spectrum (*ax*: blue, *eq*: red) compared to the experimental spectrum (black). Efforts for the determination of precise equilibrium structures will be shown as well.



B_J/MHz	1805.746	1362.268
B_K/MHz	1399.699	3143.384
B_-/MHz	163.861	169.238

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Contributed speaker MD1
Monday, September 2, 11:00
Chair: J.-U. Grabow
Room D
Fundamental physics

Observation of predissociative Rydberg states in a high-density molecular plasma

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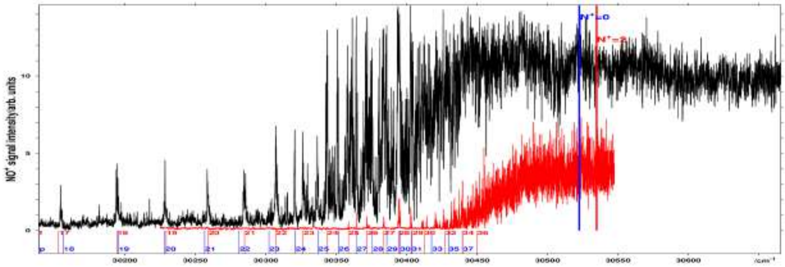
A long life-time ($> 0.3\,\text{ms}$) ultra-cold molecular Rydberg plasma is generated by two-colour $\omega_1 + \omega_2$ threshold excitation of NO in the high-density region of a pulsed supersonic jet expansion of NO in neon. The intermediate rotational level ($N_\text{A} = 0$) is selected by the transition $A \leftarrow X\ Q(0)$ ($\omega_1 = 44198.9\,\text{cm}^{-1}$) and the plasma two-colour spectrum is obtained by scanning ω_2. The General Valve stagnation pressure was set to 10 bar for the black and to 3 bar for the red spectrum in the Figure. From the analysis of properties of the supersonic jet at a laser distance of 2.5 mm from the nozzle one estimates a highest NO^+ density of 10^{18} cm^{-3}. For both the black and red spectrum the molecular Rydberg plasma signal is observed over a broad range of excitation energies, from well above the ionization threshold to resolved Rydberg states well below threshold. However, in contrast to the red spectrum, which only exhibits f-levels down to $n = 24$, the black spectrum goes down to p-Rydberg levels as low as $n = 24$ and f-levels down to $n = 18$.

The lifetime of NO Rydberg states with $n = 20$, due to predissociation into neutrals, is around 1 ps for the p-series and 1 ns for the f-series. For these lower-n levels, the observed ToF NO^+ signal from the plasma depends on the competition between the rate of electron movement into the plasma versus the electron-core collision rate resulting in pre-dissociation to neutral N and O atoms. The plasma formation involves the transition from an initially unscreened Coulomb to a screened, e.g. a Yukawa potential. For the highest density, the plasma is formed directly and not via intermediate Rydberg states as in lower density plasmas produced in MOT's (10^{12} cm^{-3}, six orders lower density) or skimmed molecular beams (10^{15} cm^{-3} , three orders lower density).



Investigation of the $\nu_2 = 1$, rotation-inversion $2_{1,s} \leftarrow 1_{1,a}$ transition of ammonia trough IR–millimeter-wave double resonance

L. Juppet[1] *, O. Pirali*[1] *, Y. Liu*[2] *, M. Manceau*[2] *, B. Darquié*[2] *, O. Lopez*[2] *,*
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Metrology-grade spectroscopic measurements of molecules are of high importance for numerous applications such as testing fundamental physics [1], molecular physics [2], and astrophysics [3]. Because it is suspected to exhibit a high sensitivity to the potential m_p/m_e time variation [4], the $\nu_2 = 1$, rotation-inversion $2_{1,s} \leftarrow 1_{1,a}$ transition of ammonia at 140142 MHz is of great interest and requires to largely improve the laboratory measurements. In this context, a thorough investigation of this transition has been conducted through Doppler-free double resonance technique [5, 6, 7] using mid-infrared and millimeter wave radiations. A sub-Hz MIR QCL [8] (acting as the pump source, installed at LPL Villetaneuse) as well as a millimetre wave spectrometer (the probe radiation, provided by ISMO), both frequency-stabilised on the REFIMEV signal [9] have been used to ensure frequency metrology. Major sources of systematic shifts (such as pressure and power) have been characterized, allowing to provide bias-free experimental frequencies and their related uncertainties. In this talk, both the experimental methods and the spectroscopic results will be discussed.

References

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Cavity-enhanced spectroscopy of H_2 in a deep cryogenic regime

***K. Stankiewicz*[1] , *M. Makowski*[1] , *M. Słowiński*[1] , *K. L. Sołtys*[1] , *B. Bednarski*[1] , *H. Jóźwiak*[1] , *N. Stolarczyk*[1] , *S. Wójtewicz*[1] , *A. Cygan*[1] , *G. Kowzan*[1] , *P. Masłowski*[1] , *M. Piwiński*[1] , *D. Lisak*[1] , *P. Wcisło*[1]**

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

We introduce, for the first time, a spectrometer based on a high-finesse optical resonator operating in a deep cryogenic regime, i. e., below 5 K. This system enables uniform cooling of the entire optical cavity, including the gas sample, the mirrors as well as the piezoelectric actuator (with tunability range exceeding 20 μm [1]). The setup is designed in a way that efficiently attenuates both external vibrations and those originating from the cryocooler itself, ensuring stable operation of the optical cavity.

The spectrometer, integrated with an optical parametric oscillator (OPO), facilitates the investigation of the fundamental band of H_2 in the range from 2.2 to 2.4 μm. We will demonstrate our first measurements of the rovibrational transition $S(0)$ from 1-0 band in cold molecular hydrogen at 5 K in the Doppler-limited regime. Achieving accuracy at the level of 10^{-6} cm^{-1}, our system allows for testing of the quantum electrodynamics (QED) corrections for H_2 at the fifth significant digit of the QED correction [2, 3]. By saturating the very weak quadrupole transitions in H_2 we expect to further enhance the accuracy by an order of magnitude. This is achievable thanks to the deep cryogenic regime of our cavity and high laser power provided by the OPO.

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Probing breakdowns of the impact approximation by cavity ring-down spectroscopy: core line intensity depletion and far-wing absorption

<u>Z. D. Reed</u>[1] **, *J. T. Hodges*[1] , *H. Tran*[2] , *J.-M. Hartmann*[2]**

[1]Material Measurement Laboratory, National Institute of Standards and Technology Gaithersburg, MD City (USA), [2]Laboratoire de Meteorologie Dynamique, Ecole Polytechnique, University Paris Saclay and CNRS Paris (France)

Physically realistic lineshape models that precisely describe molecular absorption spectra are critical to accurate spectroscopic intensity and amount-of-substance determination in both laboratory and remote sensing applications. We recently employed cavity ring-down spectroscopy to demonstrate a pressure-dependent depletion of observed intensity at the core of lines and redistribution to the far wings leading to a super-Lorentzian component of the lineshape [1]. This phenomenon is not modeled in the IUPAC-recommended Hartmann-Tran Profile [2], which was derived based on the impact approximation which assumes instantaneous collision events. However, molecular dynamics simulations show that the observed intensity depletion is due to the finite duration of collisions between the absorber and collision partner. Notably, typical collision time scales are orders of magnitude shorter than the characteristic time between collisions, the latter dominating the width of homogenously broadened lines. From Fourier analysis, the resulting spectral widths from these two mechanisms scale inversely with the respective time scales. Here we present high-precision cavity ringdown spectroscopy line intensity measurements of several transitions in the (3-0) band of N_2-broadened $^{12}C^{16}O$ exhibiting trends consistent with theoretical predictions. This effect is manifest as a pressure-dependent depletion in the experimental intensity obtained by integrating over only the core region of the absorption feature and its near wings.

This mechanism, which is not currently included in molecular databases,is expected to have a significant effect on the accuracy of molecular sensing across atmospherically relevant species. Here we discuss its physical basis and how it influences far-wing line shapes.

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Vibration-rotation linelists and effective Hamiltonians from high-order canonical van Vleck operator perturbation theory

S. V. Krasnoshchekov[1] **, *I. M. Efremov***[1] **, *E. O. Dobrolyubov***[1]

[1] Department of Chemistry, Lomonosov Moscow State University, Leninskiye Gory 1-3, 119991 Moscow (Russia)

The vibration-rotation spectra can be predicted by matrix diagonalization with exact KEO and *ab initio* PES with a small subsequent adjustments to fit experimental spectra. A conceptually different inverse approach for deciphering observed linelists is based on fitting suitable effective Hamiltonians. The bridge between these theories can be built using the operator Van Vleck perturbation theory CVPT(n) that is capable to calculate linelists, spectroscopic constants and parameters of effective dipole moment operators [1, 4].

The major computational complication of CVPT(n) arises due to the necessity of calculating rotational commutators involving ladder operators of angular momentum (J_z, $J_\pm = J_x \mp iJ_y$). This problem can be efficiently solved using the normal ordering of these operators [3]:

$$
:J_z^a J_+^b J_-^c J_z^d J_+^e J_-^f: \,:=\, \sum_{k=0}^{d} \binom{d}{k} (c-b)^k \sum_{m=0}^{min(c,e)} \binom{e}{m} \frac{c!}{(c-m)!} \sum_{l=0}^{m} s(m,l) \times
$$

$$
\times \sum_{j=0}^{l} (-2)^j \binom{l}{j} (2b-c+e)^{l-j} J_z^{a+d-k+j} J_+^{b+e-m} J_-^{c+f-m}.
$$

The rotational reduction for calculation of spectroscopic constants can also be efficiently accomplished with the aid of such normal ordering. Similarly, unitary transformations of the dipole moment operator can be made using the normal ordering with the Wigner $D^1_{0,\varepsilon}$-functions ($\varepsilon = -1, 0, +1$).

The obtained effective Hamiltonian and dipole moment operators can be further used for calculation of simulated IR spectra for a chosen spectral range and vibrational transitions. A number of numerical examples for 3,4 and 5-atomic molecules is given, demonstrating the efficient of the developed approach.

References

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Contributed speaker MB2
Monday, September 2, 14:00
Chair: L. Bizzocchi
Room B
Astronomy and atmospheres

Microwave and far-infrared spectroscopy of novel species produced via high-voltage electric discharge

J. van Wijngaarden[1]

[1] Department of Chemistry, York University, 4700 Keele St W, Toronto (Canada)

The molecular composition of astronomical sources yields insights into the evolution of our Universe and can be modelled effectively by comparing astronomical observations with laboratory spectra. The most unique molecular signatures are those that involve changes in molecular rotation and occur at microwave (MW) through far infrared (FIR) wavelengths. High resolution laboratory spectra in this range are therefore valuable to establish the unambiguous molecular fingerprints of individual molecular components in complex mixtures and to derive fundamental molecular properties including geometries, dipole moments and barriers to tunneling motions. In this talk, I will describe our efforts to produce novel astrochemical targets in the laboratory using high voltage electric discharges coupled to collision-free supersonic jets (MW) and multipass absorption cells (FIR); the latter studies performed using synchrotron light from the Canadian Light Source. These preliminary studies lay the foundation for accurate descriptions of the lowest energy states of molecules needed to assign complex spectral patterns and pursue astronomical detection of novel species.

Rotational action spectroscopy of bare HCN^+ and $HCNH^+$

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Using a double-resonance vibrational-rotational scheme based on the novel leak-out action spectroscopy method [1, 2], the rotational spectra of HCN^+ and $HCNH^+$ have been measured in a 4K 22-pole cryogenic ion trap instrument. Six rotational transitions were observed for the closed-shell $HCNH^+$ cation ($^1\Sigma^+$) between 70 and 450 GHz. In comparison to previous studies [3], the low cryogenic temperature of the trap resulting in narrow line profiles allowed hyperfine splittings due to the ^{14}N quadrupolar nucleus (I=1) to be resolved for the first time in the laboratory. This hyperfine structure of $HCNH^+$ confirms the one first observed in the interstellar medium (ISM) towards the cold molecular cloud TMC-1 [4]. Furthermore, the extended set of transitions allowed the spectroscopic parameters of this important interstellar ion to be refined, including the quadrupole coupling constant eQq for ^{14}N.

For the open-shell HCN^+ cation ($^2\Pi$), we report the first pure rotational spectrum ever measured for this elusive molecule. In total, four rotational transitions of the lower energy F_1 spin-orbit component have been observed between 270 and 520 GHz. All transitions show well-resolved Λ-doubling components (e and f) each displaying extended and complex hyperfine structure due to both the ^{14}N (I=1) and H (I=1/2) nuclei. Collectively, the laboratory data obtained here will allow the first radio astronomical search of HCN^+.

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Unveil the spectroscopy of the CH_3OCH_2 radical at millimeter wavelengths using Faraday rotation acquisition method

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The detections of methyl formate (MF), and dimethyl ether (DME) in cold environments such as prestellar cores ($\leq$ 30K) [1], questions the role of gas-phase versus grain-surface chemistry processes to form Complex Organic Molecules (COMs) [2, 3]. In this context, detecting the methoxymethyl radical, CH_3OCH_2, which is thought to be a key species linking the abundances of the MF and the DME, would provide crucial information. In addition, the CH_3OCH_2 radical is expected to be a precursor of other COMs in the ISM [4].

In this study, we have carried out high-resolution spectroscopy of the methoxymethyl radical produced by the H-abstraction of DME in the gas phase [5]. This synthesis method, associated with the Faraday rotation modulation technique, allow us to record broadband spectra of the target species with a very limited number of unwanted species. This methodology is very well suited to graphical assignment procedures, such as Loomis-Wood diagram, to identify numerous series of lines broadband radical spectroscopy rapidly. We have assigned about 1000 transitions in the 160–650 GHz range, involving rotational quantum numbers N' and K_a' up to 34 and 5, respectively. These transitions were fitted using a semi-rigid Hamiltonian, providing a first set of effective experimental parameters for CH_3OCH_2 radical. In addition, we used the XIAM to fit the torsion barrier of the -CH_3 group. We obtained $V_3 = 523 \pm 2\,\mathrm{cm}^{-1}$, close to the previous value calculated by Gàmez and Senent [4]. These data were then used to predict the frequencies of the most intense lines at 10K to measure them in our set-up directly. The inclusion of these transitions (very weak at 300 K) in the dataset further constrains the model, and better supports the search for the CH_3OCH_2 radical in the ISM.

In this talk, I will present the acquisition and analysis methods as well as the spectroscopic results on the CH_3OCH_2 radical.

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High resolution rotational and rovibrational spectroscopy of H_2CCl^+

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The high resolution rovibrational and rotational spectra of astrophysically relevant chloromethyl cation, H_2CCl^+, have been measured for the first time using a 4 K cryogenic ion trap instrument employing leak-out spectroscopy [1]. Rovibrational transitions within the fundamental ν_1 parallel band (symmetric CH-stretching) were measured for the $CH_2^{35}Cl^+$ and $CH_2^{37}Cl^+$ isotopologues. In addition, the ν_5 perpendicular band (antisymmetric CH-stretching) of the most abundant $CH_2^{35}Cl^+$ species was measured also. The spectroscopic searches for the observed bands were guided by the recent report on the low-resolution spectrum of the weakly bound H_2CCl^+ – Ne complex [2]. Based on the ground state constants obtained from fits of the infrared data, twelve pure rotational transitions were measured for each isotopologue ($CH_2^{35}Cl^+$ and $CH_2^{37}Cl^+$) in the 100-250 GHz range using a novel infrared-millimeter-wave double resonance scheme involving leak-out spectroscopy [3]. The observed rotational transitions exhibit nuclear quadrupole hyperfine structure due to the presence of the ^{35}Cl and ^{37}Cl nuclei (both with $I = 3/2$). Accurate spectroscopic parameters have been derived which will enable radio astronomical searches for H_2CCl^+ in space.

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^{13}C-isotopologues of HC_3N: characterization of the first resonance system for the three monosubstituted isotopomers

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The widespread distribution of cyanoacetylene (HC_3N) in the interstellar medium (ISM) and its role in a wide range of processes give relevance to this molecule in the ISM. On the other hand, due to its large dipole moment, the corresponding molecular emissions are often optically thick. One customary way to overcome the problem is to resort to the observations of rarer isotopologues. The ^{13}C-variants of HC_3N — even in the vibrationally excited states — are thus important astrophysical tracers. Here we report on a comprehensive study of the pure rotational spectra of $H^{13}CCCN$, $HC^{13}CCN$, and $HCC^{13}CN$ in the 75–530 GHz frequency range. Using a frequency-modulated millimeter-wave spectrometer, rotational transitions spanning J values in the 9–58 interval have been recorded for the ground and the $v_7 = 1-4$, $v_6 = 1-2$, $v_5 = 1$, $v_4 = 1$, $v_7 = v_6 = 1$, and $v_7 = v_5 = 1$ vibrationally excited states. A global least-squares-fit of more than 800 newly observed transitions, together with those available in the literature [1, 2, 3], has been carried out yielding state-effective rotational constants, centrifugal distortion constants, anharmonic $x_{L(tt)}$ and $x_{L(tt')}$ constants, and ro-vibrational l-type term coefficients. The resonant system involving the $v_4 = 1$, $v_5 = v_7 = 1$, $v_6 = 2$, and $v_7 = 4$ vibrational states has been analyzed for all the species, determining the main interaction coefficients. State-of-the-art quantum chemical calculations, performed at the CCSD(T)/cc-pVQZ level of theory, provided reliable estimates for the parameters that could not be directly obtained from the fit.

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Rotational spectroscopy of deuterated species: bis deuterated glycolaldehyde and *Z*-1,2-ethenediol

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In some regions of the Interstellar Medium (ISM) the D/H ratio of molecules has been observed to be much higher than the elemental one ($\sim 10^{-5}$). The study of deuterated species is thus a precious tool for elucidating the formation mechanisms of Complex Organic Molecules (COMs) and whether they form in the gas phase or on the icy surface of interstellar dust grains. Glycolaldehyde is considered an important prebiotic molecule and it is one of the COMs which has been detected in the ISM [1] along with its enolic form (*Z*)-1,2-ethenediol [2]. Here we report on the acquisition and characterization of the rotational spectra of doubly-deuterated glycolaldehyde (CHD – ODCHO) and of the singly- and doubly-deuterated forms of (*Z*)-1,2-ethenediol (CHOD = CHOD, CHOD = CHOH and CHOH = CHOD). These species have been generated through flash vacuum pyrolysis at ca. 750°C. Our analysis covers the spectral regions between 80–115 GHz and 250–300 GHz and yielded accurate determination of the rotational and centrifugal distortion constants. These findings allowed for the calculation of an improved semi-experimental equilibrium structure of glycolaldehyde, by providing an additional set of rotational constants (those of CHD – ODCHO). Furthermore, from our results we have computed new spectral line catalogues for guiding astronomical observations.

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High resolution laboratory spectroscopy of deuterated complex organic molecules (COMs)

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Isotopologue abundance ratios are pivotal for tracing the origin and evolution of the molecular material in the process of star and planetary system formation. By following the isotopic fractionation of some crucial molecules, we now have observational evidence that the chemistry does not undergo a complete reset with the f ormation of the protostar, and hence pre-stellar cores provide the budget of matter that will finally form stars and planets [1]. In order to study the formation and inheritance of complex organic molecules (COMs) we, therefore, must also identify the associated isotopologues and their relative abundance. Our group has previously measured the laboratory spectrum of doubly deuterated acetaldehyde allowing for its first identification and uantification towards the young low-mass protostar IRAS 16293-2422 [2]. We are continuing this study into deuterated complex organic molecules, in particular methyl mercaptan (CH_2DSH/CHD_2SH), methyl formate (CH_2DOCOD/CHD_2OCOD), and methanol (CH_2DOD/CHD_2OD), where all molecules contain an asymmetric methyl rotor resulting in complex spectral patterns. I will present our efforts to collect and analyse the rotational spectrum of these species and potential searches for these species in IRAS-16293.

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Contributed speaker MC2

Monday, September 2, 14:00

Chair: A. Maris

Room C

Structure determination

Influence of the binding partner on multi-conformational species: clusters analysed by rotational spectroscopy

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Flexible molecules can adopt various conformations, determined by the fine interplay of torsional and angular strain, repulsive steric interactions, and attractive non-covalent intramolecular interactions. This balance of forces can be influenced by interactions with other molecules, resulting in changes to the conformational preferences of the monomer. The investigation of clusters in the gas phase using high resolution spectroscopic methods can provide insights on this process and its evolution as the number of partner molecules increases. In this talk, we will present several multi-conformational species of biological and atmospheric interest and their clusters, analysed by chirped pulse Fourier transform microwave spectroscopy with the aid of quantum chemical calculations. We will discuss their structures, the effect of the binding partner on the conformational preferences of the monomer, and the forces involved.

Investigation of the microsolvation of secondary organic aerosol precusors: microwave spectroscopy of nitromethoxyphenols hydrates

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Atmospheric aerosol particles significantly impact Earth's climate, with Secondary Organic Aerosols (SOAs) crucially influencing the radiative budget and cloud formation due to their hygroscopic properties and effects on atmospheric chemistry [1]. Methoxyphenols (lignin´s monomer) represent a significant part of biomass burning emissions. Recent studies demonstrate that secondary organic aerosols (SOAs) are produced through the oxidation of methoxyphenols like guaiacol and syringol. The primary oxidation products, nitro-guaiacols (NG) and nitro-syringol (NS), lead to the formation of SOAs, which respectively exhibit hydrophobic and hydrophilic properties [2]. We present here the rotational spectroscopy of 4-NG and 4-NS studied using a free jet Fabry-Perot Fourier-transform microwave (FP-FTMW) spectrometer (2 to 20 GHz) with the support of quantum chemistry calculations. Our observations on NG isomers allowed us to identify their lowest energy conformer and simulate its Watsonian rotational parameters. Each isomer shows only one planar conformer stabilized by an intramolecular hydrogen bond as already observed for guaiacol [3]. The microsolvation of 4-NG with water has been investigated, unveiling only one monohydrate complex in agreement with the demonstrated hydrophobic character of 4-NG aerosols. The study of the hydration of 4-NS, a precursor with more hydrophilic SOAs than NG is ongoing.

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Conformatonal preferences of gas-phase Gly-Gly-Gly and Ala-Ala-Ala peptides investigated with VUV-IRMPD spectroscopy and quantum chemical calculations

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Spectroscopy of gas-phase peptides provides a bottom-up approach to studying protein secondary structures at the fundamental level. Among the different spectral regions, IR spectroscopy of jet-cooled molecules, when combined with quantum chemical calculations, is a particularly sensitive tool for conformational analysis of gas-phase peptides. A traditional method to measure IR spectra of gas-phase molecules is UV-IR double-resonance spectroscopy. The advantage of this method is that it is conformer-specific, but since only 3 proteinogenic amino acid residues can act as UV-chhromophore, its application to peptides is rather limited. To overcome this drawback, we have introduced IRMPD-VUV spectroscopy which can be applied to neutral molecules of arbitrary structures, including chromophore-free peptides [1]. Our IRMPD-VUV studies performed for the two simplest homo-dipeptides, Gly-Gly and Ala-Ala, showed that both jet-cooled species prefer extended- over bent-structures in the gas phase [2, 3].

In my presentation I will show the results from our recent FELIX (Free Electron Lasers for Infrared eXperiments) experimental campaign in which we investigated conformational preferences of jet-cooled Gly-Gly-Gly and Ala-Ala-Ala tripeptides. The IRMPD-VUV spectra have also been measured in the amide-A range, which was possible due to the recent extension of the FELIX range to $\approx 3700\ \mathrm{cm}^{-1}$. The obtained spectra have been interpreted with the help of DFT calculations which suggest that, in contrast to their homo-dipeptides, both Gly-Gly-Gly and Ala-Ala-Ala assume only bent structures in the gas phase.

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Structural determination of dibenzothiophene and its water complex using broadband rotational spectroscopy

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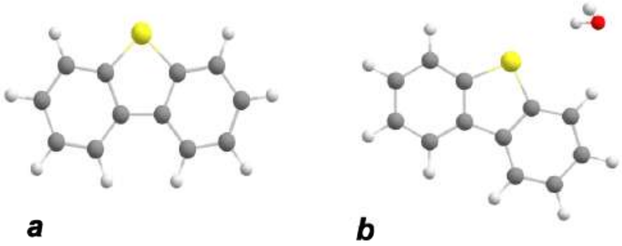
Over the past decade, chirped-pulse Fourier transform microwave spectrometers have changed the scope of rotational spectroscopy. The broad frequency coverage and large dynamic range allow for the structural determination of molecular systems of increasingly larger size due to the technique's ability to measure heavy atom (^{13}C, ^{15}N, ^{18}O, etc) isotopes in natural abundance in the same spectrum as that of the parent isotopic species [1]. In this work we study the structure of dibenzothiophene (DBT) as well as the first steps of its microsolvation via broadband rotational spectroscopy in the 2-8 GHz frequency range. We used the high sensitivity of this technique to determine the experimental atom positions and determine the substitution structure. DBT is an organosulfur compound consisting of two benzene rings fused to a central thiophene ring (see figure below). Computational methods such as B3LYP and B2PLYP with several basis sets were used to obtain the structural parameters. The accuracy of such calculations will be discussed.



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Conformations of monochloropropionic acids in gas phase and solution

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The microwave spectra of 3-chloropropionic acid (3ClPA) and 2-chloropropionic acid (2ClPA) and their water complexes have been investigated in the gas phase using Stark-modulated free-jet absorption millimeter-wave (FJ-AMMW) spectroscopy (59.6-78.3 GHz) and chirped pulse Fourier transform microwave (CP-FTMW) spectroscopy (2-8 GHz). Three conformers of 3ClPA were observed, characterized by Z-COOH arrangement. Two additional conformers of 2ClPA previously not observed [1] were found using a helium expansion. One of them is in the Z-COOH arrangement and the other one is in the E-COOH conformation and stabilized by a Cl$\cdots$H intramolecular interaction. In addition, using CP-FTMW, a 1:1 complex of 2ClPA and water in which water binds to the carboxyl group of 2ClPA, was observed in argon expansion and two complexes of 3ClPA and water were observed in helium expansion. One of these is a 1:1 complex and sees the 3ClPA forming hydrogen bonds between the carboxyl group and water and in the other 3ClPA forms a ring structure with three hydrogen bonds in a complex with a slightly distorted water dimer. All the lines exhibit nuclear hyperfine structure due to ^{35}Cl. ^{37}Cl isotopologues have been observed in natural abundance.

To investigate the behaviour of these compounds in bulk water, implicit and explicit solvent calculations were performed. The simulation of water with a continuous model suggests that the Z-COOH higher energy conformers of the molecules exhibit lower solvent free energy. This is consistent with the quantum cluster growth (QCG) [2] calculation which shows a high interaction energy with solvent molecules of these conformers. QCG calculations indicate that the solvent shell significantly influences the conformation of monochloropropionic acid, specifically by affecting its C-C-COH dihedral, leading to a great conformational rearrangement compared to the gas phase.

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The analysis of coupled torsional and inversion motions in weakly bounded ammonia-water complex

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We present recent updates in the measurements and analysis of the rotational spectra of ammonia-water complex in the frequency range 50 to 300 GHz using FLASH (Fast Lille Absorption emiSsion High-resolution) spectrometer coupled to a pulsed supersonic jet. The NH_3 - H_2O complex is characterized by two large amplitude motions: almost free internal rotation of ammonia owing to very low torsional barrier (around 10 cm^{-1}), and the inversion of water hindered by relatively high barrier (around 700 cm^{-1}). The rotational spectrum of NH_3 - H_2O was first analyzed using the rho-axis method Hamiltonian [1] to account for the NH_3 torsion. It allowed us to fit the data from previous studies [2], and more than 160 transitions measured in this study. Then, the "hybrid" Hamiltonian approach [3] was applied for the analysis of both torsional and inversion motions. The inversion splittings were resolved owing to the implementation of special nozzle allowing for sub-Doppler measurements. The analysis is in progress, the latest results will be presented.[2]

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[2] This work has been funded by the French National program LEFE (Les Enveloppes Fluides et l'Environnement), the ANR Labex CaPPA through the PIA under Contract No. ANR-11-LABX-0005-01, and the European project "International Network for a Research and Innovation Staff Exchange" (RISE), Marie Curie Action (call: H2020-MSCA-RISE-2019),

Contributed speaker MD2
Monday, September 2, 14:00
Chair: Q. Gou
Room D
Biology, natural substances

Simulation of vibrational signatures from the mid infrared (MIR) to the vacuum ultraviolet (VUV) range

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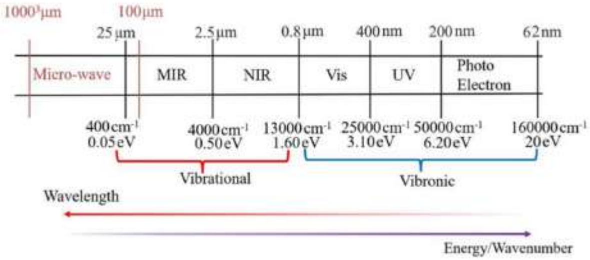
Quantum treatment of nuclear motion effects, considering either one or two potential energy surfaces (PES) within the Born-Oppenheimer (BO) approximation, allows to simulate different molecular spectra in the broad energy range [1, 2]. Approaches set within second-order perturbation theory (VPT2), accounting for the intensities of non-fundamental transitions are applied for the mid-Infrared (MIR) to near IR (NIR) range. The vibrational features determine also spectra related to the transitions between two PESs, from the visible to the higher excitation regions, which are simulated within the harmonic Franck-Condon (FC) models. The latter can be corrected for the anharmonicity employing VPT2 computations on initial and final PESs, leading to an improved agreement with experiment for the band positions.

Computational spectroscopy results will be tested against the available experimental data for systems of increasing size and complexity, from semi-rigid [3, 4] to more flexible [5] molecules, and the spectra range from the MIR (20 μm) up to the VUV (100 nm) range.



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Formation and characterization of xanthine complexes via supersonic expansion and laser spectroscopy: a comparative study with crystal sections

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Supersonic expansion allows for the formation and isolated study of complexes, free from any interference that might mask or alter intermolecular interactions. On the other hand, high-resolution spectroscopic techniques enable the acquisition of sufficiently resolved spectral lines to refine the complex structure through comparison with computational simulations. These experimental techniques provide pure information that closely approaches ideal theoretical calculations, making the data collected through these procedures highly valuable as experimental evidence.

Laser spectroscopy, specifically ion dip infrared spectroscopy (IDIRS), allows us to obtain infrared spectra of specific complexes, thereby determining their three-dimensional structure. The results obtained from these complexes can be correlated with sections of crystal structures of the same molecules. From this comparison, we can rationalize which interactions are strongest within the internal formation of the crystal and understand the initial stages of nucleation that led to crystal formation.

In particular, we will analyze xanthine complexes such as theobromine and theophylline, comparing them with stable dimers found in crystal structures available in crystallographic databases. [1, 2, 3]

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Exploring DNA derivatives hydration: IR spectroscopy studies on water interactions with theobromine and theophylline

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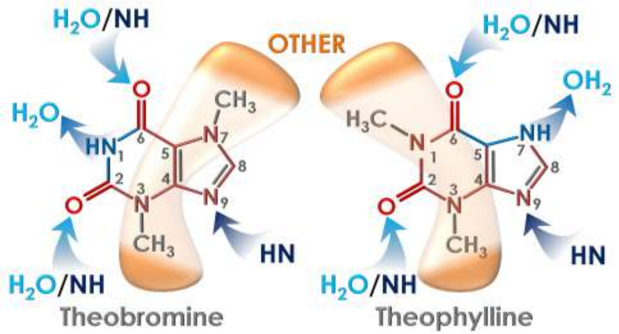
Understanding the molecular basis of life's origin is a complex research area. Although the exact conditions of early Earth are unclear, VUV radiation likely played a crucial role in promoting photochemical reactions and selecting molecules with efficient electronic excited state deactivation pathways. Intermolecular interactions were also key, as seen in the design of proteins, sugars, and nucleobases, which are structured to maximize interactions with surrounding molecules. To explore this, we studied the physicochemical properties of xanthine and its derivatives, such as theophylline (THEOP), and theobromine (THEOB). These molecules, structurally similar to DNA/RNA bases, can interfere with molecular recognition processes involving nucleobases [1].

We investigated the hydration and self-aggregation throught mass-resolved excitation spectroscopy (MRES) and density functional calculations (DFT). The obtained results highlight the specificity of the intermolecular interactions, thus giving preference to particular aggregates.



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The influence of curcumin on tau protein aggregation

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Alzheimer's disease is the most common type of dementia. It is estimated that by the end of 2050, there will be over 100 million people affected by this disease. To make things worse, we do not know not only the cure for this illness but also the exact mechanism which causes it. What is established for now is that during the progression of Alzheimer's disease, we observe pathological protein aggregation, namely deposits of amyloid β and tau protein. The inhibition of abnormal protein aggregation may result in the suppression of the development of Alzheimer's disease [1].

Characterization of this process is of the highest importance. In this research, we studied abnormal aggregation of tau protein in the presence of curcumin – a natural antioxidant. It has plenty of potential features which may be beneficial in studies of the inhibition of tau protein aggregation. To observe the influence of curcumin on the formation of tau fibrils we used complementary methods, which provided information on the morphology and structure of tau aggregates [2]. Specifically, atomic force microscopy enabled us to monitor the morphology of tau aggregates at different stages of aggregation, while spectroscopic methods gave us an insight into chemical divergences occurring due to the curcumin treatment. [3]

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Unveiling 2-aminopyrimidine: insights from rotational spectroscopy from monomer to complexes, from millimeter to centimeter wavelengths

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Pyrimidine, an aromatic heterocyclic organic compound akin to benzene and pyridine, features two nitrogen atoms at positions 1 and 3 within its six-membered ring. The enduring interest in pyrimidine derivatives for therapeutic applications stems from their often heightened activity when substituted, likely owing to their improved compatibility with receptor sites. Aminopyrimidines, particularly the 2-aminopyrimidine isomer, emerge as notable among these compounds, serving as versatile precursors for various heterocyclic compounds [1].

Our research endeavors to comprehensively examine the spectroscopic characteristics of this molecule to unveil its structure and behavior, whether in isolation or in complexation. We extensively employed high-resolution rotational spectroscopy, recording spectra at room temperature within the 75-110 GHz range. Additionally, supersonic expansion using the Fabry-Perot FTMW cavity spanning from 6 to 15 GHz was utilized, followed by the deployment of advanced chirp technology. The millimeter-wave region spectrum enabled the completion of ground state measurements and revealed various vibrational excited states [2]. The enhanced resolution measurements within the cavity enabled the resolution of hyperfine structures of the three nitrogen quadrupoles. Finally, the chirp registered spectrum (2-18 GHz) was utilized to characterize the complex formed with water, focusing on the preferential bonding point with the water molecule, nitrogen atom preferences, hydrogen bond formation, and the role of the aromatic ring.

The results obtained provide valuable insights into the chemistry of this molecule, offering potential guidance for the design of novel drugs.

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The enantioselective interactions of the carvone-1-phenylethanol complex

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The active sites of odorant receptors are sensitive to chirality. It is well known that some enantiomers of chiral odorants smell differently or have a completely different odour threshold. [1] To start gaining an understanding of the interactions involved in chirality recognition, we investigated the complex of carvone and 1-phenylethanol (1PE) using a combination of chirped pulse Fourier transform microwave spectroscopy and quantum-chemical methods. Carvone is a chiral odorant whose *R* enantiomer smells like spearmint while its *S* enantiomer smells of caraway. 1PE is a chiral alcohol with an aromatic benzene ring that can establish different types of hydrogen bonds and dispersion interactions. Several isomers of (*R*)-carvone$\cdots$(*S*)-1PE (*RS*) and (*S*)-carvone$\cdots$(*S*)-1PE (*SS*) complexes have been observed, and identified from the comparison between experimental and calculated rotational constants and dipole moment components. Carvone and 1PE are bound through an O–H$\cdots$O hydrogen bond and secondary C–H$\cdots\pi$ interactions. Homochiral *SS* complexes show an additional C–H$\cdots$O interaction. We will discuss binding preferences as well as the balance of intermolecular interactions.

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Interactions of a conformationally rich terpenoid with water: the carvone-$(H_2O)_{1-4}$ complex

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Carvone ($C_{10}H_{14}O$, 5-isopropenyl-2-methyl-2-cyclohexenone) is one of the most abundant monoterpenoids. It is present in many essential oils and used as an odorant and also released to the atmosphere from both natural and anthropogenic sources. Water is abundant in the atmosphere and in the mucus layer, and thus carvone interactions with water are of atmospheric and biological interest. We have characterised the carvone-$(H_2O)_{1-4}$ complexes using a chirped pulse Fourier transform microwave spectrometer in the 2-8 GHz frequency range in combination with quantum chemical calculations. Multiple isomers of the mono-, di-, and tetrahydrates have been observed and identified through comparison between their experimental and theoretical rotational constants and, where possible, the observation of the ^{18}O water isotopologues. Binding preferences are dictated by the formation of O-H$\cdots$O and C-H$\cdots$O hydrogen bonds. We will discuss any changes to the conformational preferences of bare carvone upon complexation as well as the accuracy of the various computational methods used.

Contributed speaker MB3
Monday, September 2, 16:30
Chair: A. Campargue
Room B
Astronomy and atmospheres

High resolution study of the ν_{22} band of pyrrole (C_4H_5N) near 14 μm

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Detecting and quantifying trace constituents of planetary atmospheres using optical remote sensing is intimately linked to the availability of reference spectroscopic information for the target species. The work reported here enters the frame of a project aiming to improve existing or provide missing line parameters or absorption cross sections for several species, selected for their relevance in planetary atmospheres. The focus is on the 600 – 2000 cm^{-1} (16.5 - 5 μm) region, relevant for current and future space missions.

Building upon the work of Mellouki *et al.* [1], the present contribution is a study of the high resolution spectrum of the ν_{22} band of pyrrole (C_4H_5N) observed near 14 μm. Five unapodized high resolution (maximum optical path difference of 600 cm, approximately corresponding to a spectral resolution of 0.0015 cm^{-1}) spectra of pyrrole have been recorded using a Bruker IFS 120 to 125 HR upgrade Fourier transform spectrometer. The spectra correspond to sample pressures ranging from 0.05 to 2.6 hPa, an absorption path length of 19.7 (2) cm and a temperature of 296 (1) K. The analysis of measured and calibrated line positions aims to better characterize the rotational structure of the upper $v_{22} = 1$ vibrational level, relying on MW data reported for the ground state [2]. Line intensities have been measured and are analyzed. Results of this ongoing work will be presented and discussed.

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Towards mid-IR quantum state-resolved spectroscopy of large molecules for astrochemistry

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The significance of large molecules, such as polycyclic aromatic hydrocarbons and fullerenes, has been growing in the fields of astrochemistry and astrophysics, as these species are candidate carriers of the unidentified infrared emission bands and diffuse interstellar bands [1]. There is an increasing need for high-resolution reference spectra to improve comparisons between simulations and observational data provided by space observatories. However, experimental studies of the spectral characteristics of large molecules are challenging due to several factors, including large rovibrational partition functions and low gas-phase sample densities.

This sets a high bar for the experimental design: high sensitivity, high spectral resolution and cooling to cryogenic temperatures are all necessary to make progress. Using cavity-enhanced frequency comb spectroscopy of buffer-gas cooled molecules, we can overcome these challenges. Here, we report on our next-generation comb spectrometer, aimed at improving upon the earlier demonstration of the quantum state-resolved spectrum of C_{60} [2]. Our optical frequency comb laser source utilizes difference-frequency generation to produce light in 6-10 μm range with 60 mW output power and 90 MHz repetition rate. To vastly increase the interaction pathlength, we couple comb light into a high-finesse enhancement cavity with length tailored for Vernier filtering. The cavity encompasses a cryogenic buffer gas cell with two-stage helium cooling and capability to produce gas-phase molecular samples through oven heating or laser ablation. We read out the comb spectrum using a dispersive spectrometer comprising a high-resolution germanium immersion grating, a cross-disperser, and a liquid-nitrogen cooled IR camera to provide low noise and fast readout. The dispersive spectrometer is complemented by a traditional Fourier-transform spectrometer, providing the advantage of effectively unlimited spectral bandwidth in a single measurement.

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The $^{15}NH_3$ ammonia spectrum between 4000 and 6350 cm^{-1}

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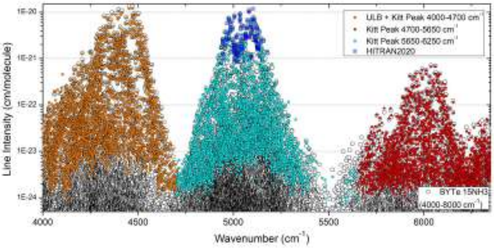
The absorption spectrum of the isotopologue $^{15}NH_3$ of ammonia is studied by Fourier Transform Spectroscopy between 4000 and 6350 cm^{-1} using both a recent spectrum recorded in Brussels, and spectra from the Kitt Peak astrophysical laboratory archive, recorded in the 90's. Overall, an experimental list including 8123 lines was retrieved for the entire region (see Figure). The ab initio calculations available in [1] and on the ExoMol website (www.exomol.com) were used to assign most of the strong lines (93% and 91% of the total experimental and ab initio intensities of the region, respectively). Lists of transitions with frequency, intensity and assignments are elaborated and proposed to improve the present status of the spectroscopic databases [2]. For instance, many lines of the $^{15}NH_3$ species with natural isotopic abundance (0.361%) should be added in the present HITRAN list of ammonia to be consistent with the HITRAN intensity cut-off of the main isotopologue, $^{14}NH_3$.



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Extended calculations of nitrogen-induced line-broadening coefficients in the ν_7 band of ethylene

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Ethylene C_2H_4 is a dangerous air pollutant, impacting plant growth and posing risks to human health. Spectroscopic monitoring of its atmospheric concentration is a method allowing to detect and reduce its emissions in order to enhance air quality. However, the current lack of both experimental and theoretical data regarding linewidths – crucial parameters for determining concentrations – necessitates massive calculations for the C_2H_4-N_2 system.

Experimental results for ethylene are extremely rare due to the molecule's polyatomic structure, resulting in dense spectra with closely spaced lines [1, 2]. To overcome these experimental challenges, theoretical calculations are an alternative. So far, the works [1, 2] simplified ethylene into a symmetric top, while the study [3] provided a rigorous treatment of C_2H_4 as an asymmetric top. However, the latter considered only the lines already studied experimentally. In addition, these calculations were, and remain, constrained by the energies available for the excited level because of the lack of analytical expressions of these levels.

Hence, this work uses the semi-classical exact trajectory model adapted to asymmetric tops in [3] to calculate 3546 broadening coefficients for transitions with the rotational quantum number J varying from 0 to 22 and $\Delta K_a = \pm 1$ (lines with detectable intensities) for the branches P, Q and R. The data produced replace the missing experimental results and are suggested to be included in spectroscopic databases (HITRAN, GEISA) for a further use in atmospheric and industrial applications.

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Assignments of methyl chloride CH-stretch overtone spectra using cross-correlation pattern recognition procedure

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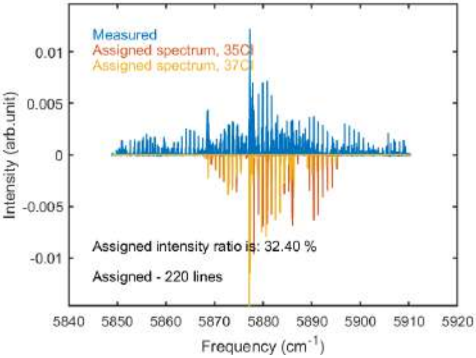
Frequent irregularities are typical in high resolution spectra of overtone and combination bands of polyatomic molecules in the near IR spectral region, caused by high density of vibrational states that mix via Fermi and Coriollis type interactions. As a result, reliable line-by-line assignments are difficult and traditional procedures based on fits to effective Hamiltonians often fail. Alternative approaches have been suggested, that utilize ground state combination differences to identify multiplets of spectral lines with a common upper level. Such procedures often provide reliable rotational labels aw well as upper state energies. [1, 2] Here we present method of cross-corelatin pattern seach, a new spectral search procedure that, unlike the previous approaches, utilizes directly the experimental spectra for multiplet identification and does not require line-list. The approach is demonstrated on previously unassigned spectrum of methyl chloride in region of the first CH-stretch overtone region.



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CRDS line-shape study of carbon monoxide (7–0) band

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Carbon monoxide, the second most abundant molecule in the universe, plays a key role in astrophysical surveys, e.g. in the analysis of the composition of the atmospheres of planets in the Solar System and exoplanets. Carbon monoxide is one of the most important molecules from the point of view of atmospheric research. It is used in monitoring pollution and transportation processes in the Earth's atmosphere. CO molecule is also an important reference point for very accurate, both experimental and theoretical, studies of spectral line intensities [2].

We present the results of line-shape measurements of the CO (7–0) band occuring near 695 nm. The spectra were acquired using the cavity ring-down spectroscopy (CRDS) technique, which is characterized by high sensitivity and stability of the frequency axis [2]. This is the first experimental observation of such high (7–0) and weak (intensities below 2×10^{-29} cm/molecule) overtone spectrum of CO. The speed-dependent Voigt profile (SDVP) was used in the data analysis. The obtained line-shape parameters are mostly characterized by uncertainties of several MHz for the line position and a few percent for the remaining parameters [3]. Agreement between the experimentally determined line intensities and the results of *ab initio* calculations based on accurate dipole moment curves and semi-empirical potential energy curves was obtained at the level of several percent, comparable to the experimental uncertainties [4].

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The O_2- and subsequently N_2-disrupted self-expansion coefficients of the ν_2, ν_5 and $\nu_3 + \nu_6$ bands of CH_3I

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Halogenated hydrocarbons have been recognized as important species in atmospheric studies. Among these halocarbons, methyl iodide CH_3I is the most abundant iodine-containing compound, emitted primarily by the oceans [1]. It is likely to play an important role in the budget of tropospheric ozone, through production of iodine by photolysis. These reasons give a great interest to measure spectroscopic parameters of this molecule. The results of such studies is of great interest to atmospheric scientists to enrich databases [2]. We have carried out the first systematic measurements of the pressure broadening coefficients of the ro-vibrational absorption transitions of the ν_2, ν_5 and $\nu_3+\nu_6$ bands of CH_3I. Spectra were recorded at room temperature (296 ± 1 K) in the spectral region between 1200 and 1600 i.e. 1300 cm^{-1} using a high-resolution Fourier transform spectrometer at the AILES beam line of the SOLEIL Synchrotron facility. The WSpectra code based on a non-linear least-squares method was used to fit a series of seven spectra at a constant pressure of CH_3I mixed with O_2 and N_2 at different pressures. The broadening coefficients were measured for numerous lines at the quantum numbers $0 \leq J \leq 70$ and $0 \leq K \leq 10$ of methyl iodide using a Voigt profiles. The average accuracies of the measurements are estimated to be about 5%. The rotational dependences of these coefficients were analyzed and modeled using an empirical model, which reproduces the measurements with a mean difference of about 7%.

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Contributed speaker MC3

Monday, September 2, 16:30

Chair: I. Kleiner

Room C

Structure determination: molecules

Low and lower: the torsional barriers of the coupled methyl internal rotations in lutidines studied by microwave spectroscopy

M. G. Barth[1] **, *S. Herbers***[1] **, *I. Kleiner***[2] **, *J.-U. Grabow***[3] **, *H. V. L. Nguyen***[1,4]

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Large Amplitude Motions (LAMs) in aromatic heterocyles are of great interest in microwave spectroscopy. For both five-membered and six-membered rings, many molecules containing one rotor have been studied [1]. The number of investigations decreases drastically for two internal rotor cases where the methyl tops are located on the aromatic rings. While there are still a handful of studies on dimethylated five-membered rings, only data on the dimethylbenzene, dimethylfluorobenzene, and dimethylanisole series are available in the literature. Investigations on dimethylated six-membered heterocycles seemingly do not exist. The lutidine (also called dimethylpyrridine) family is an example of this molecular class. Each of the six isomers contains a nitrogen heteroatom and two methyl groups acting as internal rotors.

We present here the results of two lutidine isomers, 2,4- and 2,5-lutidine. The spectra were recorded using the PARIS (chirped Pulse And Resonator In one Spectrometer) Fourier transform microwave (FTMW) spectrometer with a chirp excitation free-space cell and a single-tone excitation resonator cell, operating in the range of 2 to 20 GHz. The hyperfine structure due to the quadrupole coupling of the ^{14}N nucleus was fully resolved. The barriers to internal rotation were determined for both molecules, with the 5-methyl group of 2,5-lutidine exhibits a low barrier while the 4-methyl group of 2,4-lutidine even possesses a very low barrier. The assignments were performed with the program *XIAM* and separately fitting of the torsional species. The standard deviation of the global fits obtained with *XIAM* could be reduced significantly using the program *BELGI-*C_s*-2Tops-Hyperfine*. The experimentally deduced torsional barriers were finally compared to those of picolines (also called methylpyrridine).

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Complex hyperfine-fine structure overlapping observed in the microwave spectrum of 3,4-lutidine

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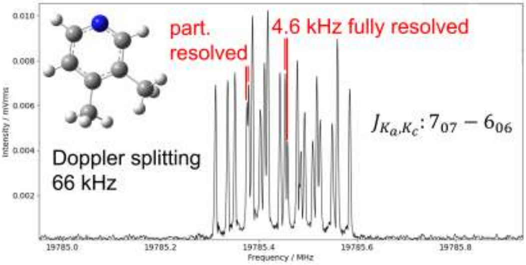
The microwave spectrum of 3,4-lutidine, also called 3,4-dimethylpyrimidine, was measured using the PARIS (chirped Pulsed and Resonator In one Spectrometer) Fourier transform microwave (FTMW) spctrometer wither a chirped excitation axis and a resonator axis, working in the frequency range from 2 to 20.0 GHz. 3,4-lutine contains two inequivalent methyl groups, causing all lines to split into quintets. These methyl groups both have intermediate barriers with similar values of 427 cm^{-1} and 508 cm^{-1}. In addition, the complete hyperfine structure including weak components arising from the nuclear quadrupole coupling of the of the ^{14}N nucleus could be observed, whose splittings are in the same order of magnitude as the torsional fine splittings. The fine-hyperfine structure combination resulted, on the average, in 25 close-lying lines for each rotational transition. Transitions with frequencies separated by larger than 3 kHz could be resolved. The program *XIAM* was used to fit a total of 529 lines, achieving a standard deviation close to the measurement accuracy. Quantum chemical calulations were performed to obtain optimized molecular geometries as well as predicted methyl torsional barriers and ^{14}N nuclear quadrupole coupling constants to guide the spectral assignment.



Exploring biaryl dithiolthiones using jet-cooled chirped-pulse microwave spectroscopy

D. Heras[1] ***, W. Li***[1] ***, M. Juanes***[1] ***, C. Pérez***[1] ***, A. Lesarri***[1]

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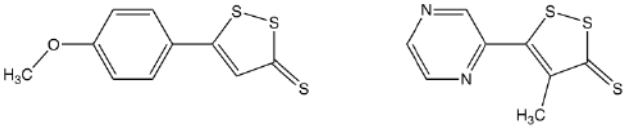
Organosulfur compounds have always been at the front of biomedical research. In this sense, dithiolthione is one of the structural motifs which hoard a major scientific interest as a strong potential pharmacophore. This fact motivates the present investigation of two therapeutic agents, anethole trithione and oltipraz, whose molecular properties, action mechanisms and structure remained unsolved with high-resolution methods.

Anethole trithione (figure, left) is a commercial drug employed for dry mouth treatment [1]. Oltipraz (figure, right) has been studied for its chemopreventive activity against various types of cancer, demonstrating efficacy in the treatment of schistosomiasis [2]. The title compounds share a biaryl assembly structure made of a dithiolthione moiety and a six-membered aromatic ring.

The rotational spectra of both compounds have been recorded with broadband chirped-pulse Fourier transform microwave spectroscopy in a supersonic jet expansion (2-8 GHz region). Two isomers were detected for anethole trithione, while the analysis of oltipraz is still in progress. Supporting quantum chemical calculations using DFT (B3LYP-D3 and B2PLYP-D3) and a triple-ζ Ahlrichs basis set (def2-TZVP) have been used to address both molecules, enabling an accurate experimental-computational determination of their molecular properties.



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The rotational spectra of 3-fluorobenzylamine: conformational analysis and tunnelling effects

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The conformational space of 3-fluorobenzylamine (3FBA) was explored employing DFT calculations at the B3LYP/def2TZVP level of theory, complete with 3D version of Grimme's empirical dispersion with Becke-Johnson damping function (GD3BJ). Varying the orientation of the lateral side chain and the position of the amino group five different conformers were obtained and further optimized at the same level of theory.

The spectra recorded in the 59.8 - 78 GHz range and 6 - 18 GHz show the presence of one conformation which, according to theoretical predictions, corresponds to the global minimum. A motion of the amino group above and below the aromatic plane, causes the μ_c-type transitions to be splitted in two components (separation of 19 MHz ca.), resulting from the interstate transitions between the rotational sub-levels belonging to two different vibrational states. Thanks to the higher resolution obtained in the lower frequency range (3 kHz) a splitting of the μ_b-type lines due to intrastate transitions was also observed. The analysis of the spectrum required the use of a coupled hamiltonian which takes into account the spectroscopic parameters, the energy separation and the vibro-rotational parameters; the quadrupole coupling of the ^{14}N nucleus was also taken in account.

A splitting of the μ_c lines was observed both for benzylamine [1] and 2-fluorobenzylamine [2] but the separation is extremely different and increases by four orders of magnitudes in going from the first molecular system (1 MHz ca.) to the second one (12000 MHz ca.). The analysis of 3FBA is thus interesting to evaluate and compare the barrier's height and tunneling pathways in the 3 systems to highlight the effects of fluorination.

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Internal rotation and structure of fluoro-substituted methyl benzoates: methyl-2-fluorobenzoate, methyl-3-fluorobenzoate, and methyl-4-fluorobenzoate

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The substitution of a hydrogen atom with fluorine in an organic compound is one of the efficient strategies for optimizing physical and chemical properties due to its small radius and high electronegativity. Indeed, the van der Waals radius of fluorine is the smallest after hydrogen (and helium) and its electron withdrawing capability not only alters the electronic properties of the compounds including dipole moments but also the molecular geometry and barriers along internal motional pathways. High resolution microwave spectroscopy combined quantum chemical calculation is an ideal tool for probing and interpreting the subtle differences in geometry and large amplitude motions.

Methyl benzoate, a common ester, finds application in various industries such as fragrances, pesticides [1] and in organic synthesis. The rotational spectra of Methyl-2-fluorobenzoate, Methyl-3-fluorobenzoate, and Methyl-4-fluorobenzoate have been investigated by high-resolution rotational spectroscopy, using a supersonic-jet expansion In Phase/Quadrature Phase-Modulation Pulse-Acquired-Coherence (COBRA)-Technique spectrometer [2], operated in the frequency ranges 6.5-26.5 GHz. Quantum chemical calculations were employed to perform conformational analyses, obtaining two, one, and one stable conformer(s) at the b3lyp-gd3bj/aug-cc-pvtz level for Methyl-2-fluorobenzoate, Methyl-3-fluorobenzoate, and Methyl-4-fluorobenzoate, respectively. The distinct mono-fluorine substation in these molecules resulted in significant structural changes and alterations in the V_3 barrier to methyl internal rotation. Our study elucidates the effects on molecular structure and dynamics, offering insights into the potential applications of fluorine substitution in optimizing chemical properties.

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Two coupled low-barrier large amplitude motions in 3,5-dimethylanisole studied by microwave spectroscopy

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3,5-dimethylanisole (35DMA) is of spectroscopic interest due to its complex large amplitude motions. The molecule features a methoxy methyl group and two methyl groups attached to the ring. The barrier to internal rotation of the methoxy methyl rotor exceeds 1000 cm^{-1}, resulting in unresolvable torsional splittings in the microwave spectrum. The low barrier heights of less than 60 cm^{-1} for the internal rotations of both the 3- and the 5-methyl groups cause large splittings [1], making the spectral assignment challenging. We will present the analysis of the complex splittings in the spectrum of 35DMA. The microwave spectra were recorded using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2.0 to 26.5 GHz [2]. Five torsional species arising from two inequivalent internal rotations were first fitted using the *XIAM$_{mod}$* program [3, 4], failing to achieve the measurement accuracy of 4 kHz for the global data set [5]. During the assignment process, the frequencies were checked by combination difference loops (Ritz cycles) to ensure the correctness of the assigned frequency. Subsequently, separate fits were carried out for each torsional species with the *SFLAMS* program [3], resulting in rms deviations of about 4 kHz, confirming the correctness of all assigned frequencies. Finally, the *ntop* program [6] was used to reduce the rms deviations to 5.5 kHz, close to the measurement accuracy. The barriers to internal rotation of the 3- and 5-methyl groups were determined to be 57.8895(21) cm^{-1} and 35.8547(19) cm^{-1}, respectively.

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Investigation and characterization of oxyamines: the rotational spectrum of diethylacetyloxyamine

F. Baroncelli[1] ***, S. Melandri***[1] ***, L. Evangelisti***[1] ***, A. Maris***[1] ***, S. Blanco***[2] ***,***
J. C. López[2]

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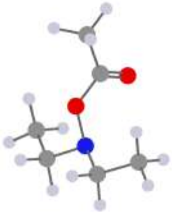
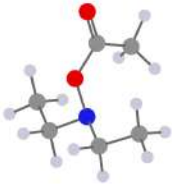
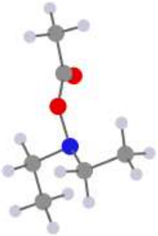
N,N-Dialkylhydroxylamine compounds are renowned for their unique properties, primarily due to the presence of the NO bond. This bond facilitates the generation of stable radicals localized on the oxygen atom, exhibiting selective reactivity towards open-shell systems. These characteristics are closely linked to the molecular structure and both inter- and intramolecular interactions within the molecule. To investigate the structural effects and properties influenced by the nitrogen monoxide sub-unit, we plan to study a series of O-substituted-N,N-dialkylhydroxylamine derivatives using rotational spectroscopy and quantum mechanical calculations. In this work we studied the rotational spectrum of diethylacetyloxyamine which has been synthesized specifically for this study as it is not commercially available. The spectral analysis covered a broad frequency range: from 6.5 to 18.5 GHz using a pulsed-jet Fourier transform microwave spectrometer, from 59.6 to 74.4 GHz via a Stark-modulated free-jet absorption millimeter-wave spectrometer, and from 2 to 8 GHz using a chirped-pulse Fourier transform microwave spectrometer. Characterization of this complex spectrum is ongoing due to the molecule's high flexibility. However, the three lowest energy conformers, along with one 1:1 water complex, have been assigned.







Contributed speaker MD3
Monday, September 2, 16:30
Chair: P. Wcisło
Room D
Atmospheres

Calculations of collision-induced line-shape parameters for N_2-perturbed lines in HF

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We report the results of the first fully quantum scattering calculations for the electric dipole R(0) transition in HF perturbed by N_2. For our quantum scattering calculations we use the 6D potential energy surface reported in Ref. [1]. Close-coupling equations are solved using BIGOS - a computational package developed in our group [2, 3], scattering S-matrices are used to calculate the generalized spectroscopic cross sections, which determine the collisional broadening and shift (and other beyond-Voigt line-shape parameters) of the N_2-perturbed R(0) line in HF. 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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Ab initio quantum scattering calculations for rotational lines in HCl perturbed by O_2

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Accurate knowledge of the spectroscopic parameters of hydrogen halides is important in the quantitative analysis of Earth's atmosphere. A particularly significant hydrogen halide is HCl, which indirectly contributes to the depletion of the ozone layer [1]. Monitoring their presence in the stratosphere can aid in characterizing the distribution of ozone and controlling the state of the ozone layer. Collisions with O_2, the second most abundant molecule in the atmosphere of Earth, perturb the spectral lineshape of other molecules, including HCl, making the interpretation of atmospheric observations challenging [2].

We report the results of the first fully quantum scattering calculations for the O_2-perturbed rotational lines in HCl molecules [3]. The calculations are performed using our new four-dimensional potential energy surface for this complex. The obtained scattering matrices (S-matrices) are used to calculate the spectroscopic cross sections, which determine line broadening and shift due to the collisions [6]. The spectroscopic parameters are derived using BIGOS – a new computational package developed in our group [4, 5]. The theoretical results show good agreement with experimental data [7, 8, 9].

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High temperature measurements of polarizability transition moments of CO_2

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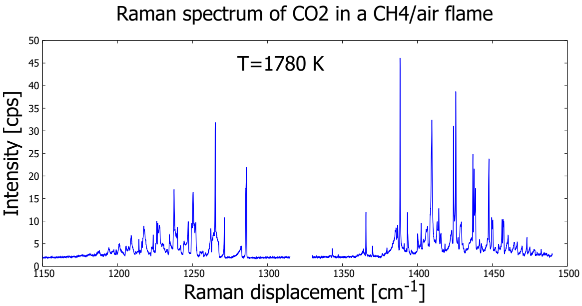
The excitation and relaxation kinetics of CO_2 is of great importance in rocky planets atmospheres, combustion, and many other processes. Raman spectroscopy is a very valuable technique to study collisional relaxation of CO_2 in supersonic jets [1]. The intensities of the Raman lines and bands stem from the transition moments of the molecular polarizability. While investigating the vibrational relaxation of hot CO_2, a lack of reliable transition moments for the many hot bands was encountered. With only a few theoretical works facing this problem [2], a precise experimental determination was acknowledged.

We present new measurements of the polarizability transition moments of CO_2 involving vibrational levels up to 3500 cm^{-1} from three different experiments, along with a reexamination of those of the fundamental bands [3].



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Databases of pressure-induced linewidths for infrared absorption by exomolecules

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Molecules and molecular ions found or expected in exoplanetary atmospheres are poorly characterized from the viewpoint of their spectroscopic line-shape parameters. From the experimental point of view, this fact is due to elevated temperatures and high fluxes of stellar radiation impossible to reproduce in laboratory conditions. From the theoretical point of view, potential energy surfaces are unavailable and advanced (computationally expensive) calculations can not be performed. The need of accurate line shapes in addition to line intensities and positions to calculate cross-sections and atmospheric opacities has been understood quite recently [1]. Substantial efforts have been provided therefore to get at least rotationally independent estimates of pressure-broadening coefficients for vibrotational transitions lying mainly in the infrared region [2] and vibronic transitions mainly located in the UV-visible range [3] as well as advanced semi-classically calculated results for some particular molecular systems [4] and machine-learning methods to produce rotationally-dependent air-broadening data [5].

The last ExoMol-database release [6] incorporates the most reliable semi-classical estimates for more than 50 active species and 12 perturbers (Ar, CH_4, CO, CO_2, H_2, H_2O, He, N_2, NH_3, NO, O_2 and self) as well as machine-learning results for 62 active species perturbed by air. However, the values of the semi-classical estimates depend on the input interaction parameters (namely, kinetic diameters) whose available in the literature values are characterized by a quite large dispersion. To provide the users with all possible linewidth values for each molecular pair, a specialized line-broadening-oriented prototype database has been created and will be described in the present work. The choice of the minimal-temperature limits and the influence of the isotopic substitution in the active molecules will be also addressed.

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Heterodyne dispersive cavity ring-down spectroscopy for high-fidelity measurements

A. Cygan[1] *, S. Wójtewicz*[1] *, H. Jóźwiak*[1] *, G. Kowzan*[1] *, N. Stolarczyk*[1] *,*
K. Bielska[1] *, P. Wcisło*[1] *, R. Ciuryło*[1] *, D. Lisak*[1]

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The challenge of measuring the shape and intensity of spectral lines with a relative accuracy $<1‰$ is highlighted in many applications. Popular cavity ring-down spectroscopy (CRDS) can provide ultra-high precision, below 0.01‰, but its accuracy is typically no better than 10‰ due to inaccuracies in light intensity measurements [1]. To eliminate this problem, we exploit the optical frequency information carried by the ring-down cavity electromagnetic field [2]. Instead of measuring only decaying light intensity, we perform heterodyne detection of ring-downs followed by Fourier analysis to provide exact frequencies of optical cavity modes and a dispersive spectrum of a gas sample from them. Using the weak CO and HD line intensities as examples, we demonstrate the sub-‰ accuracy of our method, confirmed by the best *ab initio* results [2], and the long-term repeatability of our dispersion measurements at 10^{-4} level.

We demonstrate that our frequency-based dispersive CRDS technique has a noticeable advantage over all traditional intensity-based techniques in terms of high-fidelity of acquired molecular spectra. It allows the selection of the most linear range of a detector transfer function, thus eliminating the major contribution to the measurement error in CRDS. We point out that with a small change in configuration, any CRDS system using laser-cavity locking technology can be converted into a dispersive CRDS system, providing high accuracy and the correct frequency axis of the spectrum easily referenced to the atomic frequency standard.

Our method is a step towards improving the accuracy of many spectroscopy-based research fields, such as fundamental studies of QED in molecular systems, atmospheric remote sensing, isotope ratio metrology, thermometry and establishment of primary gas standards based on quantum properties of molecules.

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Physically grounded modeling of the atmospheric gases continuum absorption in sub-THz range.

***E. A. Serov*[1], *T. A. Galanina*[1], *A. O. Koroleva*[1], *D. S. Makarov*[1], *I. S. Amerkhanov*[1], *M. Yu. Tretyakov*[1]**

[1] Institute of Applied Physics RAS, Nizhny Novgorod, Russia

Precise knowledge of the continuum absorption of radiation by atmospheric gases is increasingly demanded by the most advanced climate and radiation models relevant to the Earth's, as well as planetary, or even exoplanetary atmospheres. Up-to-now, the measured continuum is determined empirically as the difference between the total observed and calculated resonant absorption of individual molecular lines. Under the conditions of the Earth atmosphere, binary collision approach is valid. It is possible to calculate all the components of the bimolecular continuum independently, which allows to use physically based models instead of empirical ones. The major contributors to the continuum absorption in the Earth atmosphere are H_2O – H_2O and H_2O – N_2 pairs. Contribution of N_2 – N_2 is essential in the stratosphere and for planetary atmospheres like one of Titan.

For both molecules, the continuum can be modeled as a sum of absorption by bound (stable) dimers, quazi-bound (metastable) dimers and free pairs. For N_2 – N_2 case, the model is based on the classical trajectory calculations validated by measurements in the 70–350 GHz frequency range. For H_2O – H_2O, currently known theoretical and experimental data were reanalyzed. The model for the water vapor continuum asborption was constructed using the similarity to one of CO_2 – CO_2 and CO_2 – Ar [1]. The updated analytical expressions for the H_2O – H_2O and N_2 – N_2 continua can be further used in the radiative transfer models [2].[4]

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[4] The study was supported by the Russian Science Foundation project 22-72-10118 (https://rscf.ru/en/project/22-72-10118/).

Contributed speaker TB1
Tuesday, September 3, 9:00
Chair: K. Kobayashi
Room B
Astronomy and atmospheres

New high resolution microwave and infrared spectra for atmospheric species with large amplitude motions: the case of isoprene

I. Kleiner[1] ***, S. Khemissi***[2] ***, S. Herbers***[2] ***, H. V. L. Nguyen***[3] ***, I. Gulaczyk***[4] ***,***
S. Chawananon[5] ***, P. Asselin***[6]

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Isoprene (2-methyl-1,3-butadiene), emitted by plants, is an unsaturated hydrocarbon of high abundance in Earth's atmosphere. It quickly reacts with the OH radical and is a major source of secondary organic aerosols. Isoprene also affects the oxidative capacity of the atmosphere. It has been suggested to be a biosignature marker for future observations of exoplanet atmosphere. Linelists of frequencies and intensities are highly needed. Here we will present new microwave data for *trans* isoprene using the PARIS spectrometer in resonator mode in the range 4-19 GHz combined with published data [1]. Infrared data in the 986-997 cm^{-1} spectral range recorded with a pulsed jet coupled to a mid-IR tunable quantum cascade laser spectrometer (set-up SPIRALES) allowed new assignments of the ν_{26} band compared to previous work [2]. Fitting of the ground and excited vibrational states using the internal rotor codes XIAM and BELGI will be shown[5]

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[5] This work has been funded by the French National program LEFE (Les Enveloppes Fluides et l'Environnement) and from the European Union's Horizon 2020 "International Network for a Research and Innovation Staff Exchange" (RISE), Marie Curie Action (call: H2020-MSCA-RISE-2019-872081).

Coupled methyl internal rotations with intermediate and low torsional barriers in 2,5-dimethylanisole investigated by microwave spectroscopy

H. Sun[1] **, *I. Kleiner***[1] **, *L. Ferres***[2] **, *H. V. L. Nguyen***[3]

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The microwave spectra of 2,5-dimethylanisole were measured using a pulsed molecular jet Fourier transform microwave spectrometer over the frequency measurement range of 2 to 26.5 GHz and analyzed with support from quantum chemical calculations. Only one conformer was predicted where the methoxy group and its neighboring methyl group are in *anti* positions. The two inequivalent methyl groups at the *ortho* and *meta*-positions of the anisole ring undergo internal rotations, causing all rotational transitions to split into quintets. Spectral analysis of the low torsional barrier of the *m*-methyl group with value of 56.059(22) cm^{-1} in combination with the intermediate barrier value of 445.977(98) cm^{-1} determined for the *o*-methyl group was challenging. A total of 499 torsional transitions were fitted using the computer programs *XIAM* [1] and *BELGI-C$_s$-2Tops* [2], and highly accurate molecular and internal rotation parameters could be deduced. The torsional barriers are compared to those observed for the three isomers 2,3-, 2,4-, and 3,4-dimethylanisole as well as other *o*- and *m*-substituted toluene derivatives [3, 4, 5].

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Theoretical structural and spectroscopic characterization of peroxyacetic acid ($CH_3-CO-OOH$) and dimethyl peroxide ($CH_3-O-O-CH_3$): study of the far infrared region

M. L. Senent[1] **, *S. Brahem***[2] **, *D. Missauoia***[2] **, *O. Yazidi***[2] **, *F. Najar***[2]

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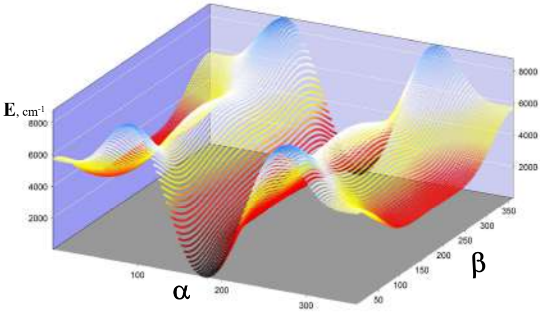
Peroxyacetic Acid [1] and Dimethyl Peroxide are two non-rigid oxygenated organic molecules which act in the atmosphere as reservoirs of HOX and ROX radicals. We present results determined using highly correlated ab initio methods with the aim of their spectroscopic characterization in the gas phase. The study focuses on the Far Infrared Region providing reliable rovibrational parameters computed using second order perturbation theory for the different conformers. Low-lying vibrational energy levels were computed variationally using a procedure that considers the interconversion of minimum energy structures. Since non-rigidity can have effects on the reactivity due to the conformer interconversion, and transitions involving low-lying levels can be observed with many spectroscopic techniques, this work can help kinetic studies and assignments of further spectroscopic studies needed for the detection in the gas phase of trace molecules.



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Extending the rotational spectrum of cyclopentadiene towards higher frequencies and vibrational states

L. Bonah[1]***, B. Helmstaedter***[1]***, J.-C. Guillemin***[2]***, S. Thorwirth***[3]***, S. Schlemmer***[3]

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Cyclopentadiene (c–C_5H_6) is a cyclic pure hydrocarbon that was already detected astronomically towards the prototypical dark cloud TMC-1 [1]. Yet, literature data of its pure rotational spectrum only covers the microwave and low submillimeter region with about 100 assigned transitions for the vibrational ground state [2]. No vibrational satellites have been reported so far.

Therefore, we extended the frequency coverage by measuring broadband spectra from 170 to 250 GHz and 340 to 510 GHz. This allowed to greatly increase the number of assigned transitions for the vibrational ground state of the main isotopologue and of the singly substituted ^{13}C isotopologues. Additionally, the rotational structure of the eight energetically lowest vibrationally excited states has been analyzed for the first time. Interactions were identified and accounted for by including Coriolis interactions in a combined fit.

The present data sets permit reliable frequency predictions of the ground states and vibrational satellite spectra far into the submm-wave range.

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Contributed speaker TC1
Tuesday, September 3, 9:00
Chair: T. D. Varberg
Room C
Combustion, catalysis, kinetics

Broadband microwave spectra of reactive intermediates

***B. A. Welsh*[1] , *T. S. Zwier*[1]**

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This talk will describe recent work in our laboratory that combines broadband microwave spectroscopy with sources that make transient reactive intermediates. Of particular interest is our studies that use a continuous, high temperature, high pressure source in which photolysis of a precursor is carried out under highly oxygenating conditions in which the chemistry can be driven towards particular reactive intermediates not easily made by other means. We will also describe initial microwave spectra of molecules, molecular clusters, and reactive intermediates in a cryocooled buffer gas cell. With these continuous sources, we signal average at 50 kHz, making it possible to record billion-shot averages in a single day. [6]

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[6] This work is supported by the Gas Phase Chemical Physics program of the Department of Energy, Office of Science, Basic Energy Sciences.

Time resolved measurements of atomic and molecular deuterium densities in a pulsed MW discharge using VUV absorption spectroscopy

N. De Oliveira[1]***, F. J. Iguaz Gutierrez***[1]***, L. Nahon***[1]***, S. Bechu***[2]***, M. Mitrou***[2]***, P. Svarnas***[3]

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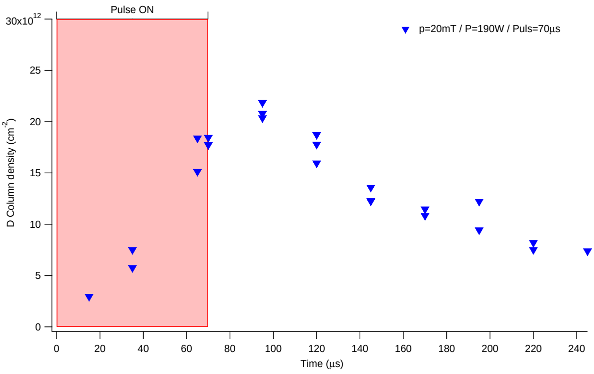
The VUV-FTS (Vacuum Ultra-Violet Fourier Transform Spectrometer) is in operation on the DESIRS beamline since 2008[1]. This unique endstation combines broad band and high spectral resolution over a large UV-VUV 300 nm - 40 nm spectral range[2]. Recently, a new detection scheme has been installed in order to study formation kinetics and decay of transient species using absorption spectroscopy. In H_2/D_2 plasmas, recombinative desorption is an effective but complex mechanism for producing ro-vibrationally excited molecules which are of interest to neutralise the highly energetic ions produced in fusion plasma, aiming at decreasing the power load on the divertor targets of tokamaks[3]. The lifetime of the produced transient species inside a pulsed MW discharge has been measured by absorption using the VUV-FTS. This data could bring valuable quantitative information for modeling such complex mechanism.



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Ultraviolet intracavity laser absorption spectroscopy

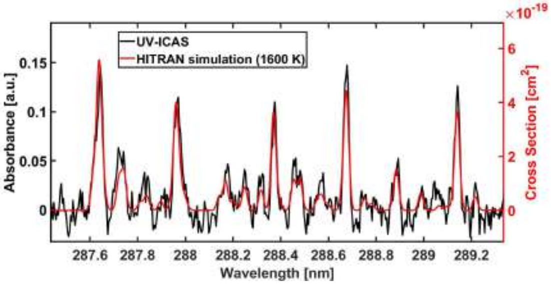
U. Zamir[1] ***, M. Cohen***[1] ***, I. Rozenberg***[1] ***, A. Lerer***[1] ***, Y. Kalisky***[1] ***, A. Kaplan***[1] ***,***
I. Rahinov[1] ***, J. H. Baraban***[1]

[1]Chemistry Department, Ben Gurion University of the Negev, 1 Ben Gurion Blvd., Beer Sheva, Israel

Intracavity Laser Absorption Spectroscopy (ICAS) provides an excellent solution for ultrasensitive, multiplexed, quantitative detection of reactive species, but has traditionally been limited to the visible and infrared spectral regions due to the requirement for direct broadband lasing media. We report the first realization of this technique in the ultraviolet (UV-ICAS), based on a home-built Ce:LiCAF laser that operates in the 280-316 nm range.

Three key species were investigated using our prototype UV-ICAS spectrometer: formaldehyde, sulfur dioxide, and hydroxyl radical. Successful initial measurements of static gases (the formaldehyde $\tilde{A}\ ^1A_2 \leftarrow \tilde{X}\ ^1A_1$ electronic transition and the sulfur dioxide $\tilde{B}\ ^1A_1 \leftarrow \tilde{X}\ ^1B_2$ electronic transition) led us to record in situ the $\tilde{A}\ ^2\Sigma^+ \leftarrow \tilde{X}\ ^2\Pi$ spectrum of hydroxyl radical in a butane flame.

Comparison of the latter to a LIFBASE simulation allowed single-shot extraction of the temperature of hydroxyl radicals in the flame, demonstrating the data acquisition efficiency of UV-ICAS. We will also discuss the technique's potential for novel ultrasensitive, high-resolution, broadband spectroscopy.



Monitoring of the synthesis and temporal evolution of tritiated methane mixtures by Raman spectroscopy

D. Diaz Barrero[1] ***, T. L. Le***[1] ***, M. Schlösser***[1] ***, H. H. Telle***[2]

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Tritium, the radioactive isotope of hydrogen, is an indispensable reagent for future tokamak-type nuclear fusion reactors (like the International Thermonuclear Experimental Reactor, ITER). It also is the key component for the Karlsruhe Tritium Neutrino mass experiment (KATRIN) at the TLK of the Karlsruhe Institute of Technology, which aims to obtain neutrino masses with higher precision. Using tritium in large quantities, radiochemical reactions take place during their circulation through the system, leading to molecular products, such as water isotopologues, Q_2O, and tritiated methane species, CQ_4 normally accumulating in low concentration (where Q can be protium (H), deuterium (D) and tritium (T).

Raman spectroscopy has become an essential analytical tool for the in-line monitoring of these gaseous mixtures. However, spectroscopic knowledge of tritiated methanes is rather incomplete, due to the very low concentrations used in the investigations to date. For the results presented here the CQ_4 compounds were synthesised in large quantities using a stepwise enrichment procedure based on catalytic isotope exchange reactions to increase the concentrations to more than 20 The resulting mixtures were composed of the family $CT_xH_{(4-x)}$, as well as the hydrogen molecular isotopologues H_2, T_2 and HT. The composition of the samples has been evaluated by depolarisation Raman spectroscopy, allowing the semi-quantification through the $\nu_1(Q_1)$ bands of the different species of the isotope-substituted methane family.

The spectroscopic data also reveal that the composition of the samples evolve over time. Complementary mass spectrometry measurements showed that several of the observed Raman signals correspond to molecules of up to 5 carbon atoms. Our preliminary analysis indicates that the radiochemical processes produce tritiated hydrocarbons with a predominance of fully tritiated ethylene.

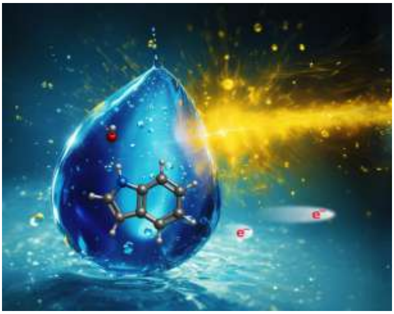
Aqueous-phase photoemission for chemical analysis

L. Tomaník[1] ***, P. Slavíček***[1] ***, B. Winter***[2]

[1]Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague, Czech Republic, [2]Department of Molecular Physics, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

Thanks to the advancement of liquid-jet photoemission spectroscopy in recent decades, [1] the photoemission of electrons from liquid samples can be systematically studied. Using bright X-ray sources at synchrotron-based facilities leads to the emission of both valence and core-level photoelectrons, as well as secondary electrons from electronic relaxation processes.

I will demonstrate how this maturing experimental technique, combined with theoretical modeling, can be used to obtain useful chemical information. Specifically, (i) I will present the probe of site-specific acid-base structure in the example of the glucose molecule. (ii) The probe can be extended even to two specific acid-base sites simultaneously, and it can reveal the tautomeric form in the solution, as I will demonstrate on vitamin C. (iii) Photoelectrons contain information about specific solute-solvent interactions, as revealed in our study of indole schematically shown in Fig. 1. [2] (iv) Secondary electrons provide unprecedented insight into the first solvation shell and its composition, illustrated with the ATP-Mg^{2+} interaction.



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Contributed speaker TD1
Tuesday, September 3, 9:00
Chair: O. Asvany
Room D
Laser spectroscopy

Mass-correlated, high-resolution rotational Raman spectra

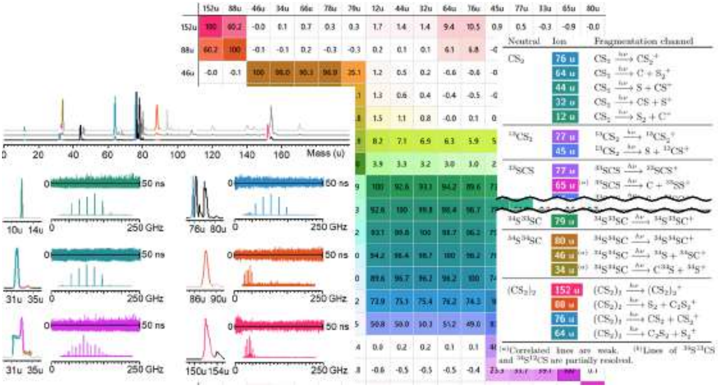
T. Schultz[1] **, *B. R. Özer*[1] , *I. Heo*[1] , *J. C. Lee*[1]**

[1] Departments of Chemistry, Ulsan National Institute of Science and Technology, 44919 Ulsan (Korea)

Mass-correlated rotational alignment spectroscopy (CRASY) is a pump-probe experiment, using an ultrafast laser pulse to excite a coherent superposition of rotational states via impulsive Raman excitation and to then probe the resulting state superposition by photoionization. Interference between rotational states leads to delay dependent signal oscillations, which are Fourier-transformed to obtain mass-correlated rotational Raman spectra.

As in any interferometric measurement, the achievable spectral range and resolution is determined by the delay range and step size. Scans with 1 ps step size and $> 1\mu$s range delivered sub-MHz resolution across a 500 GHz spectral range, well beyond the performance of other scanned interferometers.

CRASY data is of particular value for the analysis of heterogeneous samples. Data for a CS_2 molecular cluster beam allowed us to assign 28 distinct parent-fragment correlations for the molecular dimer and for naturally occurring isotopologues of the monomer. The experimental data, analysis, and interpretation is illustrated in the figure below: (Left, top) The mass spectrum shows signals for ionized CS_2 clusters, molecules, and fragments. Offset, grey traces have 22 and 500-fold enlarged ordinate. (Left, bottom) Delay dependent signal modulations and Fourier-transformed spectra for selected ion signals. (Center) Pearson correlation table: high correlation values of mass-correlated spectra indicate parent-fragment relationships. (Right) Partial list of assigned fragmentation channels for CS_2 clusters and isotopologues.

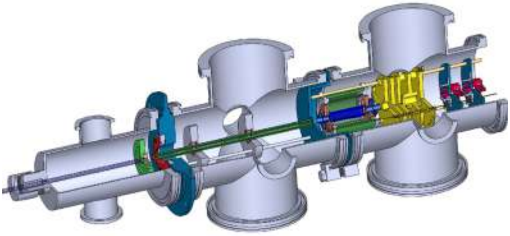


Development of 14-pole RF ion trap equipped with electrospray ion source high resolution time of flight mass spectrometer

M. Selvaraj[1] , **U. Kadhane**[1]

[1] Department of Physics, Indian Institute of Space Science and Technology, Trivandrum, 695547 Kerala, India

The recent observations of nitrogenated aromatics sparked the need to understand their stability under UV radiation in neutral as well as protonated forms. To decipher the molecular dynamics of the protonated nitrogen-containing aromatics, a 14-pole RF ion trap mass spectrometer equipped with an electrospray ion source is built in the AMP lab, IIST. This instrument is to be utilised to comprehensively investigate the stability and dissociation mechanisms of small protonated nitrogen-containing aromatic compounds. The trapped ions will be cooled down to a lower temperature using He buffer gas as well as liquid nitrogen. The temperature-controlled trapped ions will then be mass-selected and dissociated by a nanosecond pulsed laser in a wide range of wavelengths from UV to IR. The ions then will travel through a parallel plate energy analyzer where they will be energy analyzed and detected by a position-sensitive detector. The high-resolution energy selective time of flight mass spectrum will provide the dissociation trends of the astronomically significant nitrogenated aromatics in protonated form.



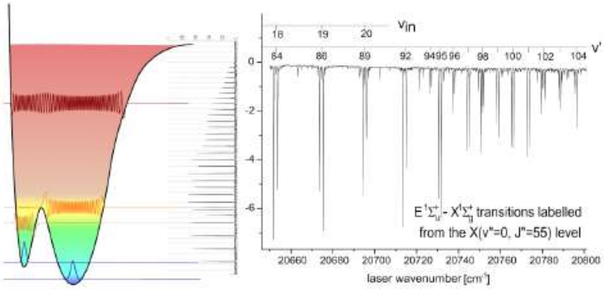
The 3D mechanical design of the ESI-Ion trap mass spectrometer

The complete energy selective high resolution 14pole RF Ion trap Time of flight mass spectrometer at AMP Lab, IIST

The double minimum $E\,^1\Sigma_u^+$ state in CS$_2$

W. Jastrzebski[1], **J. Szczepkowski**[1], **P. Kowalczyk**[2], **A. Pashov**[3]
[1]Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw (Poland), [2]Institute of Experimental Physics, Faculty of Physics, University of Warsaw, ul. Pasteura 5, 02-093 Warszawa(Poland), [3]Faculty of Physics, Sofia University, 5 James Bourchier blvd., 1164 Sofia (Bulgaria)

The double minimum $E^1\Sigma_u^+$ state in caesium dimer was investigated by analyzing spectra of the $E^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ band system, simplified by polarization labelling. Transitions to the regions below and above the internal potential barrier can be easily distinguished by a distance of consecutive PR doublets. Quantum numbers v denote absolute numbering of the vibrational levels, whereas labels v_{in} correspond to independent numbering only of the levels supported by the inner well. The inner well of this state was already partially described by Amiot et al. [1]. Currently a total of 6727 rotationally resolved transitions to levels situated in the inner well and above the internal barrier were identified and a potential energy curve allowing to reproduce their energies was constructed using the Fourier grid Hamiltonian and inverted perturbation approach methods. The unambiguity of the potential curve in view of lack of data related to levels located in the outer well is discussed [2]



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IR-UV double resonance spectroscopy of formaldehyde. Part I: revealing new vibronic levels of the $\tilde{A}\,^1A_2$ state

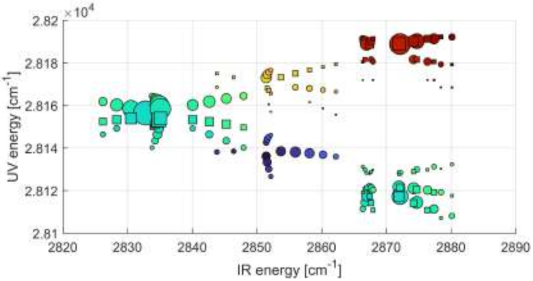
***N. Genossar-Dan*[1] *, M. Cohen*[1] *, E. Brudner*[1] *, J. H. Baraban*[1]**

[1] Chemistry Department, Ben Gurion University of the Negev, 1 Ben Gurion Blvd., Beer Sheva, Israel

Electronic spectroscopy of formaldehyde (H_2CO) has had a significant impact on our understanding of various concepts in the molecular physics of polyatomic molecules, from Coriolis coupling to the pseudo Jahn-Teller effect. Although the $\tilde{A}$-state of formaldehyde has been investigated for many years, it remains incompletely characterized, mainly due to the forbidden nature of the $\tilde{A}\,^1A_2 \leftarrow \tilde{X}\,^1A_1$ transition.

IR-UV double resonance spectroscopy enables the observation of bands typically inaccessible or difficult to analyze; the spectra are significantly simplified by the combined selection rules for both transitions, easing the assignment of newly detected levels.

In this series of two talks, we will present new results observed in IR-UV double resonance LIF spectra of formaldehyde, including detection of the ν_1 and $\nu_4 + \nu_5$ levels of the $\tilde{A}$-state for the first time. In this first part, we will discuss the experimental aspects of the study and the analysis of the rovibronic structure of the observed bands.



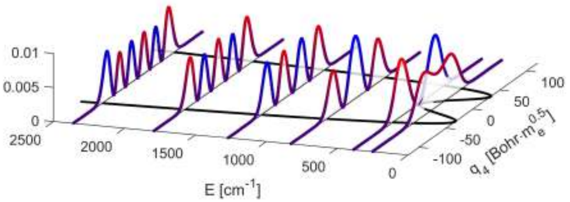
IR–UV double resonance spectroscopy of formaldehyde. Part II: the effect of vibronic coupling on cross anharmonicities

N. Genossar-Dan[1] **, *M. Cohen***[1] **, *E. Brudner***[1] **, *J. H. Baraban***[1]

[1] Chemistry Department, Ben Gurion University of the Negev, 1 Ben Gurion Blvd., Beer Sheva, Israel

The $\tilde{A}\ ^1A_2$ state of formaldehyde (H_2CO) is strongly affected by pseudo Jahn-Teller interaction with the $\tilde{B}\ ^1B_2$ state. This vibronic effect leads to several significant consequences, including distortion of the C_{2v} symmetry and creation of a double-well potential in the out-of-plane bending coordinate q_4, which is reflected in the highly anharmonic level structure of the ν_4 vibration. The same vibronic interaction is also the source for the intensity borrowing that permits the $\tilde{A}\ ^1A_2 \leftarrow \tilde{X}\ ^1A_1$ transition.

In this second talk, we analyze newly detected and assigned vibrational levels in the light of this vibronic interaction, with emphasis on the cross-anharmonicity between ν_4 and the stretching modes ν_1 and ν_5. We compare the results to models of varying complexity to extract maximum insight: these models span from a simple parameterized Hamiltonian incorporating a linear vibronic term and harmonic vibrational terms, through a one-dimensional discrete variable representation (DVR) treatment using an effective *ab initio* potential energy surface (PES), to a fully dimensional vibrational model. Our results shed light on the interplay between spectator modes and the tunneling dynamics induced by vibronic coupling.



Contributed speaker TB2
Tuesday, September 3, 11:00
Chair: M. Melosso
Room B
Astronomy and atmospheres

Insigths from numerically exact approaches for the calculation of the rovibrational energy structure of tri- and tetratomic molecules

M. Mladenović[1]

[1] MSME, Univ Gustave Eiffel, UMR 8208 CNRS, 77454 Marne-la-Vallée, Cedex 2, (France)

Numerically exact rovibrational calculations are valuable tools for achieving a complete (full-dimensional) physical description of molecular behavior for e.g. a given potential energy surface constructed within the Born-Oppenheimer approximation. Methods for such calculations, which I have been developing for general tri- and tetratomic molecules, use the exact body-fixed kinetic energy operator in combination with flexible basis sets and efficient computational strategies. No approximation beyond the concept of the potential energy surface is made, that is, no dynamical approximations and no re-expansion of the potential energy function are applied.

The determination of molecular equilibrium structures, which is one of the key goals of spectroscopy, will be first addressed. Geometric parameters are unambiguously deduced only from equilibrium rotational constants, which are unfortunately not directly accessible experimentally. For the derivation of such structures, we have designed a two-step experimental-theoretical procedure based on numerically exact rovibrational energy levels. This approach will be described in more detail for the case of HCO^+, HOC^+, and HN_2^+ [1, 2].

Another example of using calculated energy levels is the evaluation of the partition functions over a wide range of temperatures. This will be illustrated for AlOH, whose partition functions are needed to assess the role of AlOH in the formation of the first dust grains in oxygen rich stars.

To obtain the maximum information possible in rovibrational calculations, a good functional representation of the potential is an essential prerequisite: the fundamental symmetries must at least be satisfied. At some instaces, this request is not fulfilled by commonly used quartic force fields based on near-equilibrium arrangements. This will be discussed for OAlOH, an example of quasilinear molecules.

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The semi-experimental equilibrium structures of small radicals and an extension to larger species

S. Alessandrini[1] **, M. Melosso**[1] **, L. Bizzocchi**[1] **, C. Puzzarini**[1] **, V. Barone**[2]

[1] Department of Chemistry "Giacomo Ciamician", Via F. Selmi 2, I-40126 Bologna (Italy),
[2] INSTM, via G. Giusti 9, I-50121 Firenze, (Italy)

The semi-experimental (SE) approach is a useful tool to obtain highly accurate equilibrium structures for molecules in their isolated form. Within such an approach, the experimental rotational constants of different isotopic species are combined with computed vibrational and electronic corrections to obtain the SE equilibrium rotational constants. Then, these are employed in a least-squares-fit to derive the SE equilibrium structure of the molecule [1].

Even if this tool was proposed in 1978 [1] and has been vastly employed for closed-shell species [2, 3], only recently it was systematically applied to radicals with the aim of developing a small dataset for benchmarking purposes [4]. During my contribution, the main outcomes of this systematic investigation will be discussed, pointing to the lack of experimental data as well as critical aspects to consider when dealing with radical species. To extend the accuracy of the SE approach to larger species, the SE equilibrium structures of the dataset have been employed within the so-called “Lego-brick” approach [5], deriving also accurate predictions for unknown systems, like $C_{10}S$ and the naphthyl radical.

References

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An *ab initio* spectroscopic model of the carbon monoxide molecule

M. Khalil[1], N. El-Kork[1], R. P. Brady[2], S. N. Yurchenko[2], J. Tennyson[2], S. J. Evans[3]

[1]Khalifa University, College of Physical Sciences and Engineering, Abu-Dhabi, United Arab Emirates, [2]Department of Physics and Astronomy, University College London, London, WC1E 6BT, United Kingdom., [3]Computational Physics, Inc., Springfield, VA, USA

The CO molecule is known to be of high importance in applications related to medicine, environmental studies and astrophysics [1, 2, 3]. Investigations related to its electronic structure go back to as early as the start of the 1900's with the first recordings of infrared bands [4, 5]. Since then, the absorption and emission spectra of ro-vibrational levels among different electronic states have been thoroughly investigated [6, 7]. Surprisingly, however, some of the higher energy bands in the UV region are still theoretically less characterized. In this work, we present a new *ab initio* spectroscopic model for the ground and electronically-excited states of the Carbon Monoxide molecule. The model is obtained through *ab initio* calculations at the CASSCF/MRCI+Q level. We concentrate on the less investigated higher energy electronic bands such as $B\,^1\Sigma^+ - X\,^1\Sigma^+$, $C\,^1\Sigma^+ - X\,^1\Sigma^+$, and $E\,^1\Pi - X\,^1\Sigma^+$. The last two bands are of high importance for the analysis of spectral data acquired by spectrophotometers onboard spacecrafts such as the Emirates Ultraviolet Spectrometer on the Emirates Mars Mission HOPE probe [8]. We illustrate how these bands are used for better analyzing the composition of the Martian atmosphere [9].

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Towards a strict diabatic representation for coupled *N*-state diatomic systems: total rovibronic equivalence

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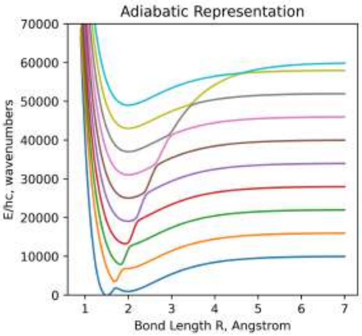
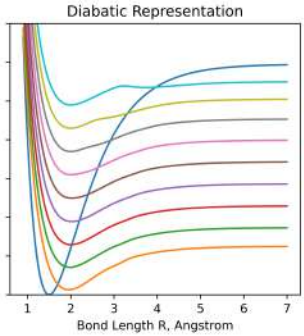
Traditionally, the (stationary) Schrödinger equation for atomistic systems is solved using the adiabatic approach, which is both practical and effective for predicting near-equilibrium properties of many molecules. Non-adiabatic effects, significant when electronic state interactions become important, are incorporated through derivative couplings (DDRs), or non-adiabatic couplings (NACs). For diatomic systems, the adiabatic representation shows avoided crossings between potential energy curves (PECs), while the diabatic representation, achieved by removing the DDRs, offers an alternative approach where PECs cross and diabatic couplings (DCs) ensue.

We demonstrate a numerically-exact diabatising transformation for the general *N*-state coupled system and show (for the first time) numerical equivalence between the adiabatically and diabatically computed rovibronic solutions. We showcase equivalence for 2-, 3-, 4- and a synthetically generated 10-state diatomic systems. Our results highlight the importance of both first and second-order DDRs and indicate that the convergence of vibronic energies depends on the chosen representation. Rovibronic energies and wavefunctions are computed using a new diabatic module implemented in our variational rovibronic code DUO (https://github.com/Trovemaster/Duo).





VUV and UV-Vis FT-spectroscopy of CO: analysis of the unimolecular interactions

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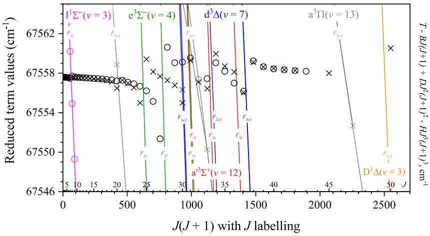
The vast majority of astronomical research is based solely on the results of precise atomic and molecular spectroscopy [1, 2]. In order to ensure high accuracy of the CO measurements, two complementary HR spectroscopy technics were used: VUV-FT (the DESIRS beamline at synchrotron SOLEIL, France [4]) and UV/VIS-FT (1.71-m Bruker spectrometer IFS-125HR, University of Rzeszów [5]).

The results were subjected to multi-level deperturbation analysis based on the effective Hamiltonian and the method of simultaneous determination of molecular constants and term values implemented into the PGOPHER program [6]. This allowed for a complete description of the energy structure of CO electronic states by taking into account both homogeneous and heterogeneous, extensive and multi-state, direct and indirect interactions.

$^{13}C^{18}O\ A^1\Pi(v=2)$



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Accessing all vibrationally excited states of the $X^+\,^2\Sigma_u^+$ ground electronic state of He_2^+ through multi-step laser excitation

M. Holdener[1] ***, H. Schmutz***[1] ***, J. A. Agner***[1] ***, M. Beyer***[2] ***, F. Merkt***[1]

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Precise spectroscopic measurements in small molecular systems such as He_2 and He_2^+ is of significant interest as benchmark to *ab-initio* quantum-chemical calculations [1, 2, 3]. In the case of He_2^+, only the lowest ($v^+ = 0-2$) [4, 5] and very highest ($v^+ = 21-23$) [6] vibrational levels of the $X^+\,^2\Sigma_u^+$ electronic ground state have been characterised experimentally. In this talk, we describe a method to access all vibrational states of He_2^+ $X^+\,^2\Sigma_u^+$ from $v^+ = 0$ to $v^+ = 23$ using a multi-step excitation scheme. The approach involves the production of a supersonic beam of He_2 in the long-lived metastable a $^3\Sigma_u^+(v = 0-2)$ states through an electric discharge. A pulsed laser promotes the system to a selected excited vibrational level of the c $^3\Sigma_g^+$ electronic state with v' in the range $3-5$. These states predominantly decay radiatively to the a $^3\Sigma_u^+$ state with $v \geq v'$ because of favorable Frank-Condon factors. A second laser is then employed to induce transitions from these vibrationally excited a $^3\Sigma_u^+(v)$ metastable states to vibrationally excited He_2^+ $X^+\,^2\Sigma_u^+(v^+ \geq v)$ states. High-resolution photoelectron spectra of these ionizing transitions are recorded using the technique of pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. In another experiment, the second laser is used to directly photoionise the intermediate state c $^3\Sigma_g^+(v', N')$ to the state $X^+\,^2\Sigma_u^+(v^+, N^+)$ levels and record PFI-ZEKE photoelectron spectra. With these excitation schemes, spectra of $X^+\,^2\Sigma_u^+(v^+, N^+)$ rovibrational levels of He_2^+ could be measured for the first time from the ground ($v^+ = 0, N^+ = 1$) rovibrational level all the way up to the dissociation limit. These new results will be compared with the predictions of *ab-initio* quantum-chemical calculations.

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Contributed speaker TC2
Tuesday, September 3, 11:00
Chair: C. Pérez
Room C
Instrumental technique demonstration

A high-performance tunable THz source for spectroscopy and more

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M.-A. Martin-Drumel[2] **, *R. Kassi***[3] **, *G. Ducournau***[3]

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The field of THz waves is booming, with a wide variety of applications ranging from imaging and telecommunications to radar and spectroscopy. These advances have been largely driven by progresses in electronic frequency multiplication chains using powerful microwave amplifiers. However, this up-conversion approach is hampered not only by the losses induced by each frequency multiplication, but also by the associated increase in phase noise, which degrades the emission linewidth.

An alternative approach involves down-conversion from the optical domain, typically by mixing two near-infrared laser sources in a photomixer to generate THz waves from the frequency difference. The phase noise associated with this process is independent of the frequency generated. It results essentially from the combination of the phase noise of each of the lasers.

Until now, the phase noise of laser sources has been insufficient to compete with electronic sources. Here, we present a two-laser source that takes advantage of the optical feedback of a high-finesse cavity to propel standard telecom lasers to unprecedented levels of stability [1]. The photomixing of this pair of lasers generates a tunable wave between 100 GHz and 1.4 THz, with a spectral width of less than Hz and a relative stability of $5 \cdot 10^{-14}/s$.

To illustrate the source's performance, we'll be showing very high-resolution spectra of gas-phase molecules we have recorded, with their frequency axes linked to international standards. Sub-Doppler structures are resolved, illustrating the spectral purity of the emission, the finesse of the tunability and the fact that the generated THz power is sufficient to induce optical saturation of the transitions. Finally, we present a series of results obtained by exploiting the very low phase noise of this source to support telecommunications transmissions using QAM modulation at very high data rates.

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Raman thermometry of confined gas micro-flows

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Microfluidics devices with internal gas flows are nowadays subject of a rapid development. However, there is a lack of experimental techniques capable of measuring the internal properties, such as temperature, in gas flows confined in small channels [1].

Raman spectroscopy is a powerful non-intrusive technique to probe gas jets at the molecular level with high spatial resolution, as we have demonstrated in the Laboratory of Molecular Fluid Dynamics of the IEM [2].

Here we present a proof-of-concept application of Raman thermometry to the gas flows within the millimetre-sized channels. For this work, we have designed several channels with forced thermal gradients, and demonstrated that the gas temperature in the flow can be retrieved, with high spatial resolution, from the rotational and vibrational Raman spectra of molecules like N_2, CO_2 and acetone [3].

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Benchmarking a reduced-footprint broadband microwave spectrometer for simplified structure characterization

***A. Byars*[1] *, S. Shipman*[1] *, R. Sonstrom*[1] *, J. Neill*[1]**

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We will describe the performance of a novel chirped-pulse microwave spectrometer for the characterization of molecular structures in the 200-300 amu mass range. The spectrometer covers the frequency range of 7-18 GHz, with a user-selectable bandwidth of up to 2 GHz. Two sampling inlets can be integrated with the system, one a modified GC inlet and the other a headspace inlet, both with fully automated sampling introduction. The chirped pulse is amplified by a pulsed solid-state amplifier with approximately 8 watts of output power. The primary goal of this instrument is to make characterization of new molecular structures by microwave spectroscopy increasingly routine and straightforward. In this talk, we will discuss the performance of this instrument and its relative sensitivity compared to both theory and our larger 3-nozzle broadband spectrometer across a series of commercially available molecules, including 4-cumylphenol, celestolide, and traseolide. Challenges related to the computational chemistry of molecules in this size range will also be discussed.

Towards electronic spectroscopy of mass and shape selected cationic metal carbides in the context of diffuse interstellar bands

C. Rossi[1] ***, B. Gans***[1] ***, U. Jacovella***[1] ***, Y. Žabka***[2] ***, J. Jašík***[2]

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The Diffuse Interstellar Bands (DIBs) are a set of more than 600 absorption features observed ubiquitously in the interstellar medium (ISM). More than a century after the discovery of the first DIBs, all but four remain unattributed, and C_{60}^+ is still the only known carrier [1]. Large carbonaceous species are ideal candidates because their size, characterized by a large number of vibrational degrees of freedom, enables them to efficiently cool down without dissociating in the harsh radiation environment of the ISM. However, as the number of atoms in these species increases, the number of stable isomers becomes extremely important, preventing an exhaustive study of their spectroscopic characteristics. This calls for new strategies for identifying carriers of the DIBs.

We propose a three-step strategy that consists in 1) identifying and isolating the magic structures (species exhibiting peculiar thermodynamic stability such as C_{60}^+ [2]) ; 2) performing exploratory spectroscopic work ; 3) recording spectra of the bare ions. Our method utilizes a custom-designed instrument that combines cutting-edge mass and ion mobility spectrometry with two complementary laser spectroscopic methods.

We are presently engaged in the first step, targeting the cationic metal-containing carbon clusters (metal carbides), which are attractive DIBs carrier candidates. Indeed, cosmic metals are abundant [3] and capably favor peculiar molecular structures exhibiting high thermodynamical stability. Preliminary mass and mobility spectra will be presented.

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Chirped pulse and resonator in one spectrometer (PARIS): a supersonic-jet chirp and tone fourier transform microwave spectrometer for broad acquisition and high resolution.

H. V. L. Nguyen[1] ***, S. Herbers***[1] ***, S. Khemissi***[1] ***, M. Schwell***[1] ***, I. Kleiner***[2] ***, X. Landsheere***[2] ***, J.-U. Grabow***[3]

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Supersonic-jet Fourier transform microwave (FTMW) spectroscopy is a powerful tool for studying isolated gas-phase molecules where an extremely low rotational temperature near the thermodynamic zero point can be reached. The classical coaxial resonator-jet spectrometer arrangement provides unrivalled resolution, but suffers from repetitive, time-consuming frequency retuning of an high-Q resonator to acquire survey spectra. The chirp-excitation method, which employs a short but powerful frequency-ramp signal passing through molecular resonances, can reduce the survey time dramatically, but at the cost of lower resolution and sensitivity, such that many microwave laboratories are using both spectrometers. With both machines needing a vacuum system capable of handling the jet-expansion at appreciable repetition rate as well as high-frequency electronic and computerized control set-up, this tends not only to be expensive but also requires turn-over time. We developed and implemented an FTMW spectrometer capable of both techniques with an innovative and resource-efficient approach: Using a smart design, most electronic components will be used in dual-purpose while integration both jet-expansion setups in a single vacuum chamber. The tone- and chirp-excitation setups are arranged perpendicularly in the spherical chamber of a single instrument named PARIS, operated in either mode with instant turn- over. Both, the high-resolution and the broadband arrangements of PARIS, use a microwave propagation coaxial with the molecular jet-expansion. Currently, PARIS achieves a sensitivity of a few parts-per-billion (ppb) of OCS diluted in Neon (1%) on the resonator axis and a few parts-per-million (ppm) on the broadband axis. A resolution (full width at half mean, FWHM, of the amplitude spectrum) of about 3 kHz and 9 kHz can readily be achieved with the high-resolution and broadband experiments, respectively, capable of resolving the complex hyperfine structures arising from two ^{14}N nuclei of 4-methylpyrimidine already in broadband operation.

Using new DC-discharge sources to investigate the formation of benzonitrile

A. L. Steber[1] **,** ***C. Pérez***[1] **,** ***J. R. Morán***[1] **,** ***F. Sajeev Hussain***[1] **,** ***I. Peña***[1] **,**
A. Lesarri[1]

[1] Department of Physical and Inorganic Chemistry, Faculty of Sciences – I.U. CINQUIMA, University of Valladolid, Paseo de Belén 7, E-47011 Valladolid (Spain)

The presence of polycyclic aromatic hydrocarbons (PAHs), their size, and their distribution in the interstellar medium (ISM) have been a topic of much debate in the recent past. However, the detection of cyclic species, starting with benzonitrile in 2018 [1], in the TMC-1 cold molecular cloud have given us new insight into these questions. Several of these species have been cyano-derviatives of a pure PAH, such as the isomers of cyano-naphthalene [2], which act as proxies of the pure hydrocarbon form. Because of their seeming prevalence, it is important to understand the chemistry that can be occurring to form such cyano-derviative PAHs. Thus, we have designed and built a new DC-discharge nozzle to pair with a broadband chirped-pulse Fourier transform microwave spectrometer that allows us to probe different formation reaction mechanisms. While the chemistry of benzonitrile in a typical discharge experiment has been studied [3], we use this new design to further probe the reaction mechanisms that may be occurring.

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Contributed speaker TD2

Tuesday, September 3, 11:00

Chair: F. Tamassia

Room D

Linelists and datasets

PYCKETT and LLWP – new tools to increase the efficiency of SPFIT/SPCAT

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SPFIT and SPCAT are two programs for "the fitting and prediction of vibration-rotation spectra with spin interactions" introduced by Herbert M. Pickett over 30 years ago [1]. Since then they have established themselves as versatile workhorses of spectroscopic analysis. Here, we present two recently developed tools written in Python to increase the efficiency of working with SPFIT/SPCAT: Pyckett and LLWP [2].

Pyckett is a library wrapping SPFIT and SPCAT allowing to read, write and manipulate the typical SPFIT/SPCAT in- and output files as well as running SPFIT/SPCAT virtually. Built on this framework are command-line utilities for performing typical tasks, e.g. to test which additional parameter would improve the fit the most or which parameter can be omitted without degrading the fit noticeably.

Luis' Loomis-Wood Program (LLWP) is a software based on Loomis-Wood plots [3] for exploring and assigning spectra. Its graphical user interface makes it very user-friendly and allows for confident and efficient assignment. Furthermore, LLWP provides easy access to a variety of tools for evaluating the analysis, e.g. inspecting the residuals and quantum number coverage or checking the strongest yet unassigned predictions.

A brief overview of Pyckett and LLWP will be given and we will highlight their independent and combined use-cases in recent analyses of molecules.

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Revisiting the $0-0$ and $1-0$ bands of the $A-X$ system of CrH with PGOPHER

A. J. Ross[1] ***, P. Crozet***[1] ***, A. Genoud, J. Morville***[1]

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We have recorded transitions in the A $^6\Sigma^+$–X $^6\Sigma^+$ system of CrH in laser excitation, and in cavity-enhanced absorption. Laser excitation experiments used a single mode, tuneable Ti:sapphire laser (Sirah Matisse) for the 0-0 and 1-0 bands. The high-sensitivity absorption experiment combines a high-finesse optical cavity with a mode-locked Ti:sapphire laser (Kapteyn-Munane Labs Chinook) frequency comb as a light source, and uses Vernier filtering. The cavity optics are optimised near 775 nm, so only the 1-0 band has been recorded this way to date. Part of the excitation spectrum has also been recorded in magnetic fields up to 0.45 Tesla. Although few features can be fully resolved with Doppler-limited spectroscopy at 500K, Zeeman profiles are often well-defined, and we noted that many 'satellite' lines of negligible intensity in the zero-field spectrum become quite strong at magnetic fields above 0.2 Tesla.

We used Western's PGOPHER program [1] first to fit the zero-field spectrum, and then to predict the magnetic response of CrH, taking starting parameters from papers by Bernath and co-workers [2, 3, 4]. Strong perturbations in the 0-0 band arise from mixing with an unobserved a $^4\Sigma^+$ state, and the 1-0 band region is even more complicated, with ^{53}CrH contributions becoming distinguishable from those of the dominant ^{52}CrH species. It is hard to recognize the branch patterns for the six spin-components; assignments were attempted using term-value fits rather than the usual effective Hamiltonian. The cavity-enhanced absorption spectrum also shows evidence of transitions to one component of the B $^6\Pi$ state in the same spectral region.

One aim of this work was to produce reference spectra for the CrH bands seen in (often magnetically active) cool stars. Predictions from PGOPHER were compared with spectra recorded at ground-based telescopes [5], and gave successful matches.

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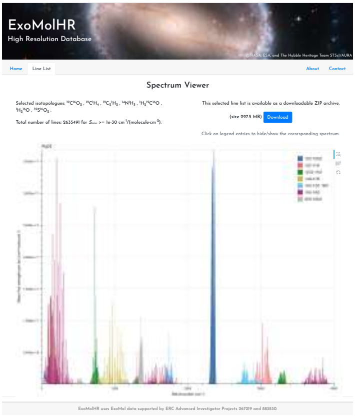
ExoMolHR: a relational database of empirical high-resolution molecular spectra

J. Zhang[1] , ***J. Tennyson***[1] , ***S. N. Yurchenko***[1] , ***C. Hill***[2]

[1] Department of Physics and Astronomy, University College London, UK , [2] International Atomic Energy Agency, Vienna, Austria

ExoMolHR is a database of empirical high resolution molecular spectra calculated using high temperature molecular line lists from the ExoMol molecular database for modelling exoplanet atmospheres. The recommended datasets in the ExoMol database store comprehensive and highly accurate spectral line lists, with uncertainties, generated through the MARVEL procedure [2], from which the data used in the ExoMolHR database are derived. The ExoMolHR database is freely accessible for calculating intensities at different temperatures in specified wavenumber ranges and plotting spectra on its website `https://www.exomol.com/exomolhr/`. The cross sections can be calculated with the Python program PyExoCross [2]. ExoMolHR currently provides data for 33 molecules and 58 isotopologues [3], these numbers will grow with updates of the main ExoMol database.



Spectrum Viewer

Selected isotopologues: $^{12}C^{16}O_2$, $^{12}C^{1}H_4$, $^{12}C_2{}^{1}H_2$, $^{14}N^{1}H_3$, $^{1}H_2{}^{12}C^{16}O$, $^{1}H_2{}^{16}O$, $^{32}S^{16}O_2$.

Total number of lines: 2635491 for S_{min} >= 1e-30 $cm^{-1}/(molecule \cdot cm^{-2})$.

This selected line list is available as a downloadable ZIP archive.

(size 297.5 MB)

Click on legend entries to hide/show the corresponding spectrum.

ExoMolHR uses ExoMol data supported by ERC Advanced Investigator Projects 267219 and 883830.

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Assignment of measured spectra with the MARVELous methane line list

K. Kefala[1], ***A. Owens***[1], ***S. N. Yurchenko***[1], ***J. Tennyson***[1]
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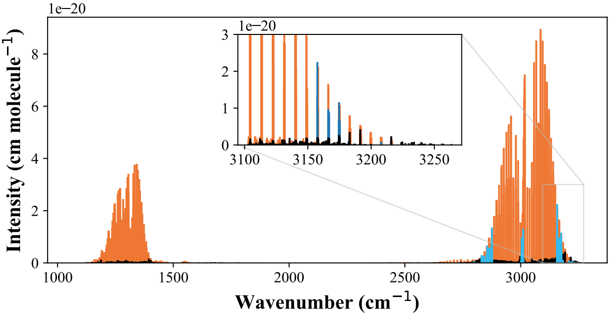
The ExoMol methodology was used to produce the recent ExoMol MM (MARVELous Methane) line list [1]. Over 50 billion transitions were calculated with the variational program TROVE [2] and improved by incorporating empirical energy levels computed with the MARVEL algorithm [3] from assigned measured transitions and associated uncertainties collected from the literature [4]. The MM line list is key in assigning quantum numbers to a collection of unassigned methane spectra, across a range of temperatures and from approximately 140 experimental sources collected from the literature. These unassigned spectra, which cover the wavenumber range of 1000 to 13000 cm^{-1}, include several polyad bands and are either partially or entirely unassigned. In assigning these spectra, new energy levels are determined using the MARVEL procedure, and the quality of the MM methane line list is iteratively improving. The figure below illustrates the spectrum by [5].



Orange indicates 8547 lines assigned with MARVEL transitions, blue shows 172 lines aiding in deriving 157 new energy levels, and black represents 3661 unassigned lines

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Spectroscopic constants from rovibrational configuration interaction calculations

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Molecular (ro)vibrational spectra from microwave, millimeter wave and infrared experiments are usually represented by rotational and centrifugal distortion constants. These spectroscopic constants are derived from (and usually computed by) perturbation theory. In experiment, transition line lists are taken as reference for fitting an effective Hamiltonian, turning the constants into fit parameters. These constants (or parameters) concisely grasp the essence of a spectrum and, thus, are indispensable when it comes to communication of spectroscopic results.

While "experimental" spectroscopic constants are derived by fitting, their *ab initio* calculation is often based on vibrational perturbation theory (VPT). However, it is well-established that variational approaches, e.g., rovibrational configuration interaction (RVCI), are superior in calculating rovibrational states. Thus, spectroscopic constants from RVCI are desirable.

We here present a procedure, using RVCI [1] calculated rovibrational states and transitions as a reference for fitting Watson's A- or S-reduced Hamiltonian including up to sextic centrifugal distortion [2, 3]. Based on an educated parameter guess from VPT, our procedure becomes very efficient. First tests on small asymmetric top molecules (water, hydrogen sulfide, formaldehyde and thioformaldehyde) show very good agreement with experimentally derived spectroscopic constants [4].

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Measurements and modeling of line parameters for the ν_3, $\nu_3 + \nu_6 - \nu_6$ and $2\nu_3 - \nu_3$ bands of methyl fluoride at 10 μm

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FT experimental spectra of natural CH_3F have been analyzed around 10 μm where the strong absorption of the ν_3 band can be observed. This band is approximately 10 times stronger than the ν_6 band located nearby around 1200 cm^{-1}. The ν_6 band has been previously studied [1] and is present in the HITRAN and GEISA databases contrary to the strong ν_3 band absent from these databases. In this work, we present mainly measurements and a band-by-band analysis of absolute line intensities (never measured before) of ro-vibrational transitions belonging to the strong ν_3 band as well as to weaker $2\nu_3$ - ν_3 and ν_6 + ν_3 - ν_3 hot bands of $^{12}\mathrm{CH_3F}$. Moreover the ν_3 of $^{13}\mathrm{CH_3F}$ has also been observed and studied. The spectra were recorded with Fourier transform spectrometer (resolution = 0.004-0.006 cm^{-1}) at room temperature in the spectral region from 950 cm^{-1} to 1100 cm^{-1}. Then a multi-spectrum fitting technique [2] has been used to fit a series of spectra (6 pressures ranging between 0.1 and 4 mbar) using the Voigt profile. Due to the density of transitions and strong overlapping, accurate line positions from [3] have been used and fixed during the fit when transitions are unresolved. For all lines self-broadening parameters have been fixed to calculated values from [1]. Line positions measured from well resolved transitions have been compare to calculations from literature [3]. Retrieved line intensities allowed calculating the transition dipole moments squared and to observe and model its rotational behavior. Finally a line list containing transitions of the ν_3 , $2\nu_3$ - ν_3 and ν_6 + ν_3 - ν_6 bands of $^{12}\mathrm{CH_3F}$ and of the ν_3 band of $^{13}\mathrm{CH_3F}$ has been generated. Line positions are coming from calculations [3], line intensities from present work, and the self- and N_2-broadening coefficients have been modeled using the parameters obtained from [1] and [4] respectively. This line list has been proposed for the 2024 HITRAN update.

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Invited Speaker TA
Tuesday, September 3, 14:00
Chair: J. Tennyson
Room B

Ultrafast X-ray scattering: photochemical dynamics and beyond

A. Kirrander[1]

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Ultrafast time-resolved x-ray scattering provides a window onto the dynamics induced by photoexcitation of molecules. Significant advances in resolving transient nuclear structures in excited molecules have been made. Notably, scattering provides rich information beyond molecular structure and technical developments at x-ray free-electron lasers (XFELs) enable high-quality signals with low noise. We will take stock of recent developments and discuss what experiments can be anticipated in coming years, including the computational and theoretical tools required to interpret such experiments. Detailed simulations make it possible to assess the physical insights that can be gained from different types of scattering experiments. Strikingly, the distinction between scattering and spectroscopy becomes increasingly blurred. This points towards future directions that may include the characterization of valence electronic states and direct measurements of the effects of electron correlation and coherence using x-ray scattering. Ultimately, the question is if ultrafast measurements can deliver new insights into complex photochemical and photophysical mechanisms. The answer appears positive, with scattering playing an important role.

Testing the quantum theory with accurate laser spectroscopy

P. Wcisło[1]

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The development of modern laser technologies opened the way to new and exciting research fields focusing on testing quantum theory and searching for new physics beyond the standard model. On the one hand, the key technological components are continuous wave laser systems, spectrally very narrow, with a wide modulation band, which allows them to be tightly locked to ultra-high finesse optical cavities. This provides the technological possibility of generating a laser field with very high power packed into an extremely narrow spectral range. The second key component is femtosecond lasers operating in the optical frequency comb configuration, which enable the measurement of optical frequencies with an accuracy exceeding 1 Hz. The combination of these two technologies provides an ideal tool for ultra-accurate atomic and molecular spectroscopy, i.e. it allows for generating an electromagnetic wave with a very well-defined frequency (not only spectrally narrow, but also with the controlled absolute frequency). I will talk about our projects that use these technologies for the purpose of testing quantum theory and searching for new physics. I will show the results of a project aimed at searching for dark matter and the variability of fundamental constants using optical atomic clocks [1, 2]. I will present the progress in the project aiming at testing quantum electrodynamics with ultra-accurate spectroscopy of molecular hydrogen [3].

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Poster Session 1
Tuesday, September 3, 16:30

UV-spectrum and photo-decomposition of peroxynitrous acid in the troposphere

W. Chebbi[1] ***, N. Derbel***[2] ***, A. Alijah***[3] ***, T. Cours***[3]

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The UV spectrum of peroxynitrous acid, HOONO, was computed at the B3LYP/AVTZ and MCSCF/AVTZ levels. Due to large-amplitude vibrational motions of this molecule, the maxima in the simulated spectra are displaced from the positions of vertical excitations. The three lowest excited electronic singlet states, which are all repulsive, can be reached by UV absorption. The non-adiabatic decay dynamics of photo-excited HOONO was studied using the fewest switches surface hopping algorithm inplemented in NEWTON-X. The photolysis products were determined, and the photolysis rate constant is provided for the first time. We found that near the tropopause the photolysis rate constant, $J \approx 6 \times 10^{-4}$ s^{-1} , exceeds that for thermal decomposition, $k \approx 10^{-6}$ s^{-1}, by two orders of magnitude. The photolysis lifetime is about 30 minutes. Thus, photolysis is an important process and should be included in atmospheric models [1].

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Millimeter wave spectroscopy of propenethial

K. Vávra[1] ***, L. Kolesniková***[1] ***, J. Koucký***[1] ***, G. Vylitová***[1] ***, P. Kania***[1] ***, Š. Urban***[1]

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Many sulphur-bearing molecules have been observed in the interstellar medium and circumstellar shells. Propenethial is a promising candidate for future detection. Its oxygen analogue, propenal, has already been observed [1, 2], alongside with related propynal and its sulphur analog propynethial [3]. The rotational spectrum of propenethial was investigated in the past only below 40 GHz [4]. New high-resolution measurements covering an extended frequency range from 293 to 321 GHz were conducted using the Prague millimeter wave spectrometer [5]. Essential molecular parameters for the ground state and vibrationally excited states were obtained using self written General Fitting Code. Additionally, ^{34}S and ^{13}C isotopic species were investigated in natural abundance.

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Going to higher *J* values: new measurements and assignments in the $v_t = 0, 1$ torsional states of $^{13}CH_3OH$ and $CH_3^{18}OH$

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

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We have initiated a program to investigate the torsional manifold of several isotopic species of methanol with one aim to create line lists with reliable positions and line strengths for astronomical observations and with the additional aim to analyze the intricate vibration-torsion-rotation interactions in their spectra. Here we present the results of our new study of the torsion-rotation spectra of the $^{13}CH_3OH$ and $CH_3{}^{18}OH$ isotopologs of methanol. The new microwave measurements were carried out using spectrometers in Kharkiv and Köln (in total, the frequency range from 34 GHz up to 1.1 THz is covered). The analysis is done using the rho axis method and the RAM36 program code. In our previous investigations of CD_3OH, CD_3OD, and CH_3OD we experienced difficulties to fit data for the $v_\mathrm{t} = 2$ torsional state to within experimental uncertainties. Since the emphasis of our studies on various methanol isotopologs was and still is to provide line lists for radio astronomical observations, we limited our analyses largely on $v_\mathrm{t} = 0$ and 1 in all instances. For $^{13}CH_3OH$ and $CH_3{}^{18}OH$ we also adopted this approach and at the moment we concentrate our efforts on analysis of the $v_\mathrm{t} = 0, 1$ states. In the poster the details of this new study will be discussed. [7]

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[7] This work was done under support of the Deutsche Forschungsgemeinschaft and Volkswagen foundation. The assistance of Science and Technology Center in Ukraine is acknowledged (STCU partner project P756).

Receiving system for emission spectroscopy using a matched input filter/diplexer

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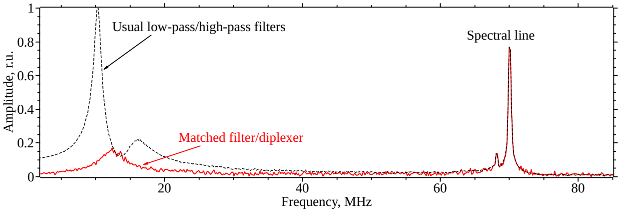
Currently, high-resolution emission spectroscopy is extensively employed for investigating molecular spectra. Molecular emission spectra are obtained from the Fast Fourier Transform (FFT) of the time-domain free induction decay (FID) after a short pulse excitation. Although the excitation and FID signals significantly differ in the frequency domain, the excitation causes considerable interference during detection. We have developed a new receiving system for a millimeter/submillimeter-wave emission spectrometer [1], which includes a matched input filter/diplexer that reduces the interference level. The figure below shows the results of applying the matched filter compared to the conventional low-pass/high-pass filtered signal. A notable reduction in low-frequency interference signals is observed in the filtered FFT spectrum. Therefore, the new receiving system enhances the exploitable frequency range for spectral analysis. [8]



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[8] The work in Kharkiv was supported by the Volkswagen foundation. The assistance of Science and Technology Center in Ukraine is acknowledged (STCU partner project P756).

Infrared absorption cross sections for isoprene in support of the exploration of planetary atmospheres

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Detecting and quantifying trace constituents in planetary atmospheres using optical remote sensing techniques is intimately linked to the availability of reference spectroscopic information for the target species. The work reported here enters the frame of a project aiming to improve existing or provide missing line parameters or absorption cross sections for several species, selected for their relevance in planetary atmospheres. The focus is on the mid-IR region, between 600 and 2000 cm^{-1} (16.5 – 5 μm), relevant for current and future space missions.

The present contribution deals with the measurement of mid-IR absorption cross sections for isoprene, the most important biogenic organic constituent on the Earth [1] and a precursor of secondary organic aerosols [2]. This spectroscopic information is measured using Fourier transform spectroscopy for mixtures of isoprene with N_2, at pressures and temperatures mimicking those found in the atmosphere of the Earth. The work carried out so far and results obtained will be presented and discussed.

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A microwave study of the oxygenated polycyclic aromatic hydrocarbon xanthene and its hydrated clusters

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Oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) have emerged as promising targets for astronomical detections, with suggestions that a C=O stretch is responsible for the 6 μm feature in infrared emissions [1]. In this study, we present a comprehensive microwave analysis of the OPAH xanthene ($C_{13}H_{10}O$) and its complexes with water. Our investigation employed broadband chirped-pulse Fourier transform microwave spectroscopy in the 2-8 GHz frequency range and quantum chemical calculations.

The structure of xanthene features three fused six-membered rings in a non-planar arrangement: two peripherial benzene rings and a central ring featuring an oxygen atom and a -CH_2 group. Its rotational spectrum exhibits a splitting of the rotational transitions into two components, generated by a tunnelling motion involving an out-of-plane bending motion of the two lateral benzene rings of xanthene. The nature of the motion was confirmed by the observation of tunnelling splitting in the rotational spectra of the singly-substituted ^{13}C isotopologues, which suggested that isotopic substitution does not break the symmetry of the motion.

The rotational spectroscopy investigation was then extended to its hydrated clusters with up to four water molecules. Different xanthene-water binding motifs are observed based on the degree of hydration, with O-H$\cdots\pi$ interactions becoming preferred over O-H$\cdots$O interactions as the degree of hydration increases. A structural comparison with related hydrated molecular systems is provided to understand the influence of the shape and composition of the substrate on the structure on the water motif.

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First analysis of the $0 - v''$ progression of the comet-tail system in $^{12}C^{17}O^+$

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

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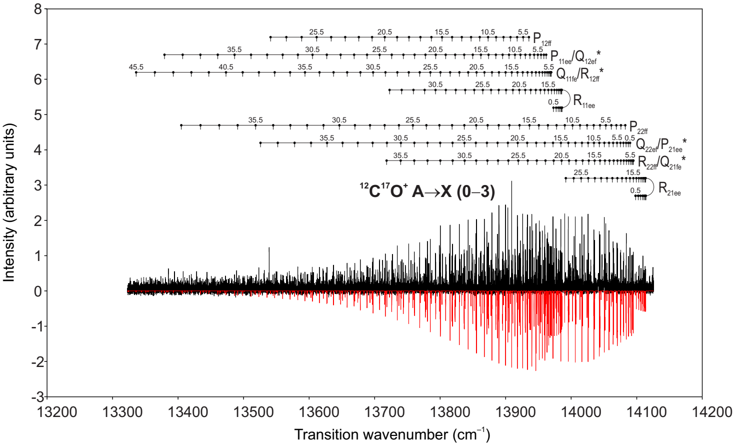
As a continuation of the studies on the $A^2\Pi_i$ state in the $^{12}C^{17}O^+$ isotopologue made by our team [1], four bands of the $0 - v''$ progression where $v'' = (0, 1, 2, 3)$ were first recorded in the emission spectrum of the Comet-Tail $A^2\Pi_i - X^2\Sigma^+$ system in the $^{12}C^{17}O^+$ isotopologue. Using a high-resolution Fourier-transform spectrometer, more than 1500 emission lines were measured in the region of 12,880 - 20,500 cm^{-1}. A deperturbation analysis was carried out with the PGOPHER program [2]. Consequently, we succeeded in determining the deperturbed molecular parameters of the $A^2\Pi_i(v = 0)$ and $X(v = 0,1,2,3)$ levels and the $A^2\Pi_i(v = 0) \sim X^2\Sigma^+(v = 10)$ perturbation parameter of a complex (spin-orbit, spin-electronic and rotation-electronic) character. The values of the ro-vibronic terms of the $A^2\Pi_i(v = 0)$ level were also calculated and the percentage $^2\Pi$ character of the $A^2\Pi_i(v = 0)$ and $X^2\Sigma^+(v = 10)$ levels was examined.



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Terahertz measurement of rotational-inversion transitions of ammonia isotopologues

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Ammonia is important astrophysical molecule as well as belongs among the most significant prebiotic molecules containing nitrogen [1, 2]. Even though ammonia itself has been measured in details practically in the most of the spectral ranges, however this does not apply to all ammonia isotopologues mainly in the terahertz frequency range.

All measurements were carried with a laser-differential spectrometer out that uses a combination of two NIR lasers with different frequencies, which are combined using the InGaAs photomixer to generate the terahertz radiation. Our study covered the frequency interval from 0.4 to 2.6 THz. The analysis brought a large number of newly measured rotation-inversion transitions, which made possible significant improvement of propriate molecular parameters. It helps us also improve the knowledge of the surrounding interstellar space and phenomena that may be happening around stars or in the atmospheres of planets that may be habitable in the near future based on ratio of ammonia isotopologues[3].

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Gas-phase conformational landscape and structure of 1-amino-indan

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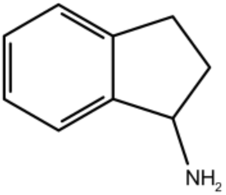
Two conformers of the 1-aminoindan molecule have been characterized in the gas phase by Chirped Pulse Fourier-transform microwave spectroscopy (CP-FTMW) in the 2-8 GHz range. Both observed conformers have an equatorial NH_2 configuration. The comparison between the experimental rotational and ^{14}N nuclear quadrupole coupling constants and those calculated by DFT and *ab initio* methods provides conclusive evidence for the identification of the conformers. The spectral analysis further allowed the observation of ^{13}C and ^{15}N in natural abundances for the most stable isomer, allowing the determination of precise structural information through the substitution (r_s) and effective (r_0) methods. Calculations on the potential energy surface have also been performed to explain the non-observation of additional conformers via collisional relaxation during the near-adiabatic expansion. A tructural comparison with indan[1] has revealed that the carbon skeleton is not substantially distorted by the introduction of the amino group.



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Line-shape parameter study of methane by a mid-infrared dual-comb spectrometer

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Remote sensing is a crucial tool to study planetary atmospheres. Radiative transfer models need various spectroscopic parameters. Among them, the line-shape parameters are the less known. On Earth, methane is the third most significant greenhouse gas. It has also been observed in atmospheres of different planets and exoplanets.

In this work, spectra are recorded with IRis-F1, a mid-infrared dual-comb spectrometer based on quantum cascade lasers. This instrument is well-suited to study precisely spectroscopic parameters [1] thanks to its high-resolution on a 60 - 100 cm^{-1} spectral range, signal-to-noise ratio and short measurement time. We study methane lines perturbed by CO_2 and N_2 at room temperature. These ν_4-band lines are located between 1285 cm^{-1} and 1335 cm^{-1}. Fitting the experimental line-shape by different theoretical profiles (Voigt, speed-dependent Voigt and Rautian-Sobel'man profiles), we determine the coefficients of collisional broadening and parameters due to fine physical effects as the Dicke narrowing and/or the speed-dependence effect. The results are in good agreement with previous literature data when available.

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High precision measurements and CRBM calculations of line shape parameters for the H_2O–N_2 collision system

B. Vispoel[1] ***, R. R. Gamache***[2] ***, N. G. Orphanos***[2] ***, K. Sung***[3] ***, G. C. Toon***[3]

[1] Research Unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur (UNamur), Namur, (Belgium), [2] Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, Lowell, MA (USA), [3] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (USA)

Laboratory measurements to H_2O transitions broadened by N_2 were made for three N_2-mixture spectra in theν_2 band at room temperature using the high-resolution Fourier transform spectrometer (Bruker IFS-125HR) at the Jet Propulsion Laboratory. The high-precision spectrum fitting package, Labfit, was used to analyze the spectra. The half-widths and pressure shifts were retrieved by fitting all the three spectra simultaneously, and holding their line intensities to the HITRAN values. Combining the N_2-broadened data with previous results for O_2-broadening [3] air-broadened data were determined. Using the pairing rules of Ma *et al*. [2] transitions were selected with pairs that agree to 1.5%. Results of the final potential fit are presented and calculations will be made to produce air-broadening data for the HITRAN database.

Government sponsorship acknowledged.

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H_2O broadened by CO_2 lineshape parameters measurements for CO_2-rich atmospheres

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Found in small amounts in Venus and Mars atmospheres, H_2O is a key-molecule in the understanding of the solar system evolution and Earth's history. Thanks to ever more improved instrumental facilities on the ground and in space, it is possible to acquire atmospheric spectra with high resolution and high signal-to-noise ratio. However, for H_2O-CO_2 collision system, air-broadening parameters are still used in many models due to a lack of spectroscopic data, which limits the precision of the atmospheric spectra. In order to contribute to the development of a list usable by the planetary community and in continuation of the article published in 2019 [1], new spectra of H_2O broadened by CO_2 were recorded at room temperature. Measurements were performed at the GSMA using the high-resolution infrared Fourier transform spectrometer coupled with a 2-meter mutlireflection cell in 2.34 and 1.17 μm spectral regions. The line parameters were then determined with a multispectrum fitting procedure using Voigt and speed-dependent Voigt profiles. While the Voigt profile is widely used for its simplicity and efficiency, it does not allow to reproduce fine physical effects visible in the laboratory measurements. The second takes into account the speed dependence of the collisional parameters, improving the fit quality, which was shown in a recent paper [2]. Finally, in the context of the next European mission to Venus, EnVision, planetary spectra were simulated. The impact of the CO_2-collisional parameters was assessed and will be presented.

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Line shape parameters for the H_2O–He collision system for astrophysical studies

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Complex Robert-Bonamy-Ma (CRBM) calculations were made for the H_2O-He collision system using an intermolecular potential comprised of Lennard-Jones atom-atom, induction, and London dispersion terms. The initial atom-atom parameters were obtained using combination rules and the other parameters from taken from the literature. The intermolecular potential was then adjusted to give results that agree with the measurements of Koshelev *et al.* [1] for the 183 and 380 GHz lines of H_2O. The final potential results (pot 35) compared with the data of Koshelev *et al.* have an average percent differences for γ of 0.83 and -0.63 percent, respectively and differences in δ of 0.000071 and -0.000027 cm^{-1} atm^{-1}, respectively. Calculations were then made for all unique rotational transitions of H_2O on HITRAN2020 [7] at 13 temperatures from 200 to 3000 K. The temperature dependence of the half-widths and line shifts were determined using the double power-law (DPL) model of Gamache and Vispoel [3] and the standard power law mode. The speed dependence of the half-width and line shift were computed for use in more advanced line shape models.

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CO_2-collisional spectroscopic parameters of acetylene lines by quantum cascade laser spectroscopy

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Acetylene is a common hydrocarbon found in Earth's and various planetary atmospheres. Its presence in our atmosphere mainly originates from anthropogenic activities such as combustion processes. In addition, C_2H_2 is found as a trace gas in the CO_2-rich atmospheres of Venus and Mars, as well as other planets and their satellites. The analysis of atmospheric spectra involves the computation of radiative transfer models that requires accurate spectroscopic data. Among them, the collisional parameters are the least well-known. The study of these line-shape parameters, such as the collisional broadening coefficients of lines, is therefore required for atmospheric studies. In 2016, Wilzewski *et al.* [1] showed that collisional parameters of acetylene broadened by carbon dioxide were not well-known and needed to be further studied. Advanced spectroscopic parameters, such as collisional narrowing and speed-dependence, can have a significant impact on the accuracy of atmospheric processes.

In this work, we determine collisional parameters of acetylene broadened by carbon dioxide in the $\nu_4 + \nu_5$ band. We study collisional broadening coefficients and their speed-dependencies, shifting coefficients and the collisional narrowing parameters by fitting advanced theoretical line-shape models such as the Rautian, speed-dependent Voigt and speed-dependent hard-collision profiles. Absorption spectra are recorded at room temperature using a homemade high-resolution dual-channel quantum cascade laser spectrometer that is well-suited for the study of line-shape parameters [2]. All measured collisional parameters exhibit a similar dependence with the J rotational quantum number. Our results are in excellent agreement with the few available data in the literature.

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Determination of $CH_4 - N_2$ intermolecular potential using modified complex Robert–Bonamy formalism — preliminary work

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Methane is an important trace gas in Earth's atmosphere as it contributes to the greenhouse effect and climate changes. Its presence has also been detected in planetary atmospheres, and is still being tracked as it is one of the proxies for life. In order to retrieve methane information from atmospheric spectra, accurate line shape parameters are needed.

In this preliminary work, the $CH_4 - N_2$ molecular system is studied using the Modified Complex Robert-Bonamy (MCRB) model [2]. This formalism has all the needed features to perform accurate calculations: high-order intermolecular potential, computation of the real and imaginary parts of the collisional cross-section, precise description of the molecular trajectory and explicit velocity integral. The intermolecular potential is composed of the electrostatic, atom-atom (expanded to high order and rank), London dispersion and induction components.

Most of the potential parameters are well-known except for the short-range interactions. The atom-atom components need to be determined by reproducing a set of high-quality experimental data. First, the influence of each atom-atom coefficient on the calculated collisional half-width was determined. Then small changes were made to them, MCRB calculations performed and the computed collisional half-widths were compared to a set of experimental data. The reference data to compare with were selected by applying an intercomparison procedure on experimental data for methane ν_4-band lines diluted in N_2. Iterations are performed until the final standard deviation of the calculated data to the experimental ones is at minimum.

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Line shape parameter prediction algorithm for the CO_2–H_2O collision system

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Using an intermolecular potential optimized for the CO_2-H_2O collision system [1], using the data of Sung *et al.* [2] (final statistics 0.11% difference and a SD of 0.993%), Complex Robert-Bonamy-Ma (CRBM) calculations were made at 13 temperatures from 200 to 3000 K for P-, Q-, and R-branch transitions with *J*" from 0-120 for vibrational bands with $\Delta\nu_1$ = 0 to 5, $\Delta\nu_2$ = 0 to 5, $\Delta\nu_3$ = 0 to 7. These data were used to solve for the coefficients giving the vibrational dependence of each rotational transition using the formalism of Gamache and Hartmann [3], which for a transition $\nu_1' \nu_2' \nu_3' f \leftarrow \nu_1'' \nu_2'' \nu_3'' i$ states:
$\gamma(\nu_1' \nu_2' \nu_3' \leftarrow \nu_1'' \nu_2'' \nu_3'')_{f\leftarrow i} = \gamma_0 + A_\gamma\ (c_1\ \Delta\nu_1 + c_2\ \Delta\nu_2 + c_3\ \Delta\nu_3)^{p_\gamma}$,
$\delta(\nu_1' \nu_2' \nu_3' \leftarrow \nu_1'' \nu_2'' \nu_3'')_{f\leftarrow i} = \delta_0 + A_\delta\ (c_1\ \Delta\nu_1 + c_2\ \Delta\nu_2 + c_3\ \Delta\nu_3)^{p_\delta}$,
where c_1, c_2, and c_3 are the coefficients of the vibrational dependence of the polarizability of the radiating molecule, and the coefficients γ_0, δ_0, A_γ, A_δ and p_γ and p_δ are the intercepts, slopes, and powers for γ and δ. A Levenberg-Marquardt non-linear least squares routine was used to determine these coefficients for each temperature studied. Once the coefficients are known, the half-width. and line shift can be determined for any ro-vibrational transition at the 13 temperatures of the half-widths and line shifts can then be determined using the double power-law (DPL) model of Gamache and Vispoel [4]. This algorithm, along with measurement and CRBM calculations, allows us to add line shape data and their temperature dependence to large databases such as HITEMP [5], AMES [6], HITRAN [7].

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Generation of line-broadening parameters for molecules in the atmospheres of hot super-earths and lava planets

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Hot super-Earths and lava worlds are a subset of rocky exoplanets that have high surface temperatures, somewhat similar to conditions exhibited by early Earth [1]. A number of these exoplanets with small radii and large masses are being detected using photometry, and follow-up spectroscopic measurements are under way [2]. However, data retrieval and theoretical modelling of those atmospheres presents certain challenges, one of which is the absence of line-broadening data. In this work, we present theoretical values of broadening parameters for molecules that might be present in those extreme conditions [4]. Calculations are performed using the Modified Complex Robert-Bonamy approach [3] with model Lennard-Jones type potentials consisting of long-ranged electrostatic interactions and supplemented by atom-atom interactions.

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The ExoMol database: developments and the 2024 data release

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The desire to characterize and model the atmospheres of the many extrasolar planets discovered over the last three decades is a major driver of current astronomy. This goal is impacted by the lack of spectroscopic data for the molecules in question since it requires significant quantities of spectroscopic data, in many cases billions of lines, to accurately reproduce the spectroscopic features of the atmospheres of hot exoplanets. The ExoMol database (`https://www.exomol.com/`) provides molecular data for interpreting spectra and modelling atmospheres of hot exoplanets and other hot astronomical atmospheres. The selected molecules are deemed to be important for exoplanets and other studies of hot atmospheres. The core of the ExoMol database is comprehensive high-temperature molecular line lists. The ExoMol line lists are systematically published as a series in the journal Monthly Notices of the Royal Astronomical Society and summarised in four-yearly release papers, with the ExoMol 2024 release being under review [1].

The recent developments in the ExoMol database include:

1. A Python program PyExoCross designed to post-process both ExoMol and HITRAN line lists [2] (`https://github.com/ExoMol/PyExoCross.git`);
2. High-resolution line list database ExoMolHR [3] (`https://www.exomol.com/exomolhr/`);
3. Adopting the IAEA (International Atomic Energy Agency) standards for the atomic and molecular information;
4. JSON format for the line list APIs (Application Programming Interface);
5. Photodissociation cross sections and continuum absorption [4];
6. Improved and extended treatment of collisional broadening;
7. The use of the MARVEL procedure to create high accuracy line lists (35+ molecules);
8. 26 extra ExoMol line lists since the 2020 release.

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Extension of the assignment of methyl formate in the low-lying vibrational excited state

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Methyl formate is a well-known interstellar molecule with over 1000 transitions identified in interstellar space, including those in the first and second torsional excited states (v_{18} and $2v_{18}$). The rotational temperatures toward Orion-KL are as high as 200 K [1]. Methyl formate also has other low-lying vibrational excited states such as COC deformation (v_{12}, 312 cm^{-1}) and skeletal torsion (v_{17}, 332 cm^{-1}) . Considering the rotational temperature, lines in these excited states will be good candidates for astronomical detection, We have shown that the rotational transitions of the vibrational excited states measured by microwave spectroscopy are COC deformation excited states by analyzing the vibration-rotation band obtained with far infrared spectrometer at the Canadian Light Source [2]. However, only low J and K states were assigned. In this paper, we report extension of the assignment.

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A heterogeneous DAC/ADC-board for chirped-pulse Fourier transform spectroscopy

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Chirped-Pulse Fourier Transform Microwave spectroscopy is a technique used to obtain rotational spectra of molecules. It offers large bandwidth, high spectral resolution, as well as high sensitivity [1]. Here, we report on the updated version of our home-built chirped-pulse spectrometer, operational in the millimeter-wave range of 75-110 GHz [2]. The detector of the spectrometer uses a heterodyne receiver built for emission spectroscopy [3] which was not equipped for sideband separation. As a result, mirror lines of rotational transitions of the molecule under study were present in the measured spectra, making assignment difficult.

To overcome this limitation, a new platform named Universal-Board (U-Board) is implemented. It has a heterogeneous architecture consisting of an FPGA and DACs/ADCs for phase-coherent signal generation and acquisition as well as rapid integration in the time domain. An onboard GPU is used to process and store the data. Several phases of excitation signals are produced and the corresponding free induction decays are measured cyclically in up to 1000 different integration frames. This data is post-processed to perform sideband separation and signal cleanup. Proof-of-concept measurements using methyl cyanide will be presented to demonstrate the advantages and sensitivity of the new instrument. Furthermore, results from applications leveraging the flexibility and versatility of the tool will be reported on.

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Absolute transition frequencies of $^{12}C_2H_2$ in the near infrared and an improved spectroscopic network at the kHz accuracy level

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We report on Lamb dip spectroscopy of $^{12}C_2H_2$, between 7125 and 7230 cm^{-1}, as performed by means of a comb-assisted cavity ring-down spectrometer (CA-CRDS). The experimental setup is an upgraded and simplified version of that already developed by our group and described in Ref. [1].

We measured the frequency of twenty transitions belonging to the P, R, and Q branches of the $\nu_1 + \nu_3 + \nu_4^1$ band, looking for *ortho* and *para* states of the molecule. Recording sub-Doppler profiles and extrapolating line center frequencies at zero pressure, allowed us to reach an overall uncertainty of about 7 kHz at 1-σ confidence level.

The selection of the investigated transitions was based on the theory of the Spectroscopic Networks (SN), so as to link, with paths and cycles, several transitions previously measured with high precision. Thanks to this approach and using a Measured Active Rotational–Vibrational Energy Levels (MARVEL) inversion procedure, 162 ultraprecise empirical rovibrational energy levels have been determined [2]. Consequently, a new line list, named TenkHz, has been generated. It contains 282 entries in the spectral range between 5899 and 7259 cm^{-1} having an accuracy which is comparable to the experimental one. Interestingly, 35 lines of the TenkHz line list are not included in the HITRAN2020 database.

Finally, we will discuss the possible extension of our spectroscopic approach to the mid-IR spectral region.

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The Raman spectrum of diacetyl revisited

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We have revisited and enlarged the vibrational analysis of diacetyl or 2,3-butanedione by means of state-of-the-art Raman spectroscopy [1] and quantum chemical computations. The Raman spectrum was obtained previously only in condensed phases [2] and hence hindered low-energy vibrational modes were undetected. Here we measured the Raman spectrum of diacetyl both in the gas and liquid phases. Some new bands have been observed for the first time. The nice agreement between the experimental spectrum and that obtained employing Born-Oppenheimer Molecular Dynamics opens the door to employ this computational tool to describe Raman intensities and vibrational frequencies in large centrosymmetric molecules.

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NO_2 reference mixtures for PEMS calibration. How much an infared spectrum can tell?

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In this work we investigate how much information a conventional infrared spectroscopic technique (FTIR) can yield for NO_2 reference materials. A simple characterization algorithm for the mixtures with NO_2 fraction between 100 and 2500 μmol/mol is developed. A set of measurements for four different mixtures at ambient temperature and varied sample pressures was performed and analysed. The proof of principles is successfully tested.

NO_2 analysers, used in the uncertainty assessment of PEMS measurement (Portable Emission Measurement Systems), are calibrated with reference materials at the amount fractions below 500 μmol/mol [1]. In this range of concentrations, the spectroscopic equipment used in this work, can reach uncertainties for low NO_2 amount fractions limited essentially by the quality of reference spectroscopic data for the monomer.

A typical FTIR spectrum of a concentrated NO_2 mixture (above 500 μmol/mol) can yield an information about NO_2 dimer and several impurities. Some of them are well-isolated and easy to analyse (N_2O, CO_2 etc.). HNO_3 proved to be the most challenging. Different assessment strategies are discussed.

The measurements and analysis were performed within the frame of the EMPIR project “Improved vehicle exhaust quantification by portable emission measurement systems metrology” (MetroPems) [2]. The spectra were recorded using a Bruker IFS 125HR spectrometer at the PTB FTIR infrastructure.

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`https://www.metropems.ptb.de/home/`

PriSpecTemp project in progress: new measurements of *A*-band of oxygen in pure gas and mixtures with nitrogen

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Oxygen is uniformly distributed in the Earth atmosphere so its absorbance it very useful for intensity calibrations in the spectra recorded by satellite and ground-based instruments in very different atmospheric conditions [1]. The oxygen A-band does not overlap with other atmospheric species, it is also very weak and do not saturate when measured over long pathlengths [2]. Knowledge of the band structure, intensities and collisional parameters is absolutely important, but remains a challenge for both theoretical and experimental investigations.

Within the frame of PriSpecTemp project [3], a set of absorption spectra of pure oxygen and its mixtures with nitrogen were recorded in the pressure range between 450 and 1100 hPa. Experimental parameters, such as pressure, temperature and path were calibrated and traceable. Extensive uncertainty evaluation for every wavenumber in every spectrum was performed. In a few intances we followed a similar procedure, used in our recent publications [4, 5] and generated composite spectra from the measurements of the same sample at different pathlengths.

The integrated absorption cross sections are in agreement with the results of previous studies. Line-by-line fits and analysis of individual parameters are ongoing. The spectra were recorded using a Bruker IFS 125HR spectrometer at the PTB FTIR infrastructure.

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Inversion splitting of the ground and some exited vibrational states of the GeH_3 radical

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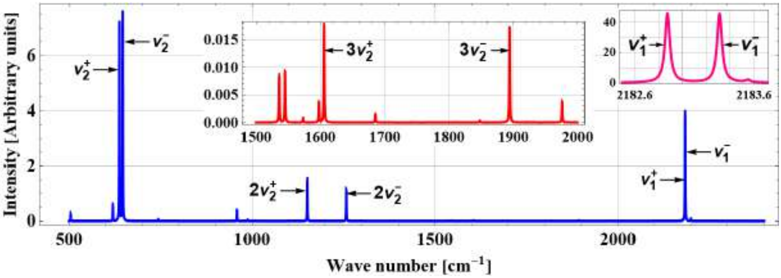
Four-atomic pyramidal molecules of the XY_3 type are of great interest. Recently, such a compounds: $^+OH_3$, $^-OH_3$, $^\bullet OH_3$ [1] and in $^-CH_3$, $^\bullet SiH_3$ [2] were analyzed. Our attention was focused on ν_2 and ν_1 totally symmetric vibrational modes. The original set of vibrational coordinates was used, including the distance from X atom to center of the regular triangle H_3 and totally symmetric coordinate composed from three distances between hydrogen atoms. Using this approach in current work the $^\bullet GeH_3$ radical was investigated. The 2D potential energy surface was calculated at the CCSD(T)/dAug-cc-pVQZ level of theory. Then, by solving the 2D vibrational Schrödinger equation, the values of the energies of the ν_2 and ν_1 modes of the $^\bullet GeH_3$, as well as their inversion splittings, were found. Our calculations show that inversion splitting of the ground vibrational state is equals to $0.216\,cm^{-1}$ and for ν_2 and ν_1 modes we have got next values: 637.8 and $646.7\,cm^{-1}$ for $^+\nu_2$ and $^-\nu_2$, 1151.0 and $1257.3\,cm^{-1}$ for $2^+\nu_2$ and $2^-\nu_2$, 1606.3 and $1894.2\,cm^{-1}$ for $3^+\nu_2$ and $3^-\nu_2$, 2183.1 and $2183.4\,cm^{-1}$ for $^+\nu_1$ and $^-\nu_1$ respectively. The corresponding IR spectra for the analyzed modes are represented at Figure.



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The experimental NH_3 line-list in the 6000-8000 cm^{-1} range.

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The present contribution provides an overview of our recent progress in completing the experimental line-list for the ammonia molecule in the infrared range. Following a similar approach to our previous studies [1, 2, 3] in the $3900 - 6350$ cm^{-1} range, we present the current state of processing additional spectra recorded during our earlier works [3, 1]. To provide a comprehensive line list based on these datasets, special care was given to *(i)* verification of the assignments and correction of discrepancies present in the published line lists, *(ii)* identification of $^{15}NH_3$ transitions with intensity larger than 10^{-23} cm/molecule, *(iii)* providing the “best possible" line intensities with respect to existing studies.

This research was supported by the Slovak Research and Development Agency (APVV-19-0386) and Scientific Grant Agency (VEGA-1/0710/24).

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The electronic spectrum of gas-phase niobium hydride, NbH

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We have recorded and rotationally analyzed six different electronic transitions of the molecule NbH by laser excitation spectroscopy using a hollow cathode discharge source. The bands cover the wavelength region 575–650 nm. All of these bands are assigned as $\Omega = 0$–0 transitions, which indicates that the electronic ground state is likely to be $\Omega = 0$, in agreement with MCSCF calculations by other workers. By least-squares fitting, the ground state rotational constant was determined to be $B_0 = 4.9717\,\mathrm{cm}^{-1}$, in close agreement with the MCSCF results. This value yields a ground state bond length of $r_0 = 1.844\,\text{Å}$. Further work is underway to search for more transitions in the red and near infrared using a continuous-wave Ti:sapphire ring laser.

Spectral similarities for molecular structural identification via rigorous analysis of a new benchmark database

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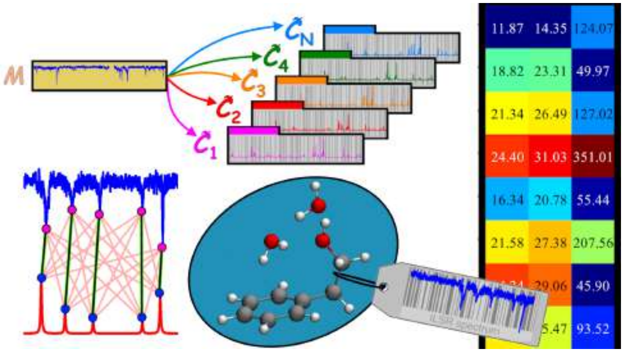
Vibrational spectra, monitoring structural-sensitive features, offer valuable insights into molecular structures, bonding, and dynamics. Yet, interpreting the measured spectra and identifying the structures requires theoretical equivalents and quantitative metrics. We address these challenges by creating a new experimental database of broad-range ionization-detected stimulated Raman scattering signatures and harmonic Raman frequencies calculated by widely used density functional methods/basis sets. Comparing these results allows us to derive single global and multiple frequency-region- and mode-dependent scaling factors, revealing the latter's superiority. Additionally, we utilize Euclidean/Manhattan distances (EDs/MDs) among measured and predicted features to obtain cost matrixes and then apply the Kuhn-Munkres (KM) assignment to evaluate the minimal one and retrieve corresponding matching spectral barcodes. The resulting KM-ED/MD or optimal transport average distances rank spectral similarities, and the former even identify structures. This new approach quantitatively solves the spectral assignment problem, revealing subtle structural alterations, and is anticipated to benchmark future predictions.



Spectral analysis and density profiling of the small organic molecules in protostellar sources

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The study of small organic molecules in star-forming regions is crucial for understanding the complex processes that lead to the formation of stars and planetary systems. In this work, we present a spectral analysis and density profiling of small organic molecules in a sample of Class 0 and Class I protostellar sources obtained with the Northern Extended Millimeter Array (NOEMA) interferometer. The aim is to determine the distribution and abundance of small organic species such as $C^{17}O$, ^{13}CO, SO and others. The NOEMA data provide high spatial resolution (1-2") and high sensitivity, which are crucial for resolving and quantifying the abundances of these key molecular tracers. The detected species are important precursors to more complex organic molecules.

Rotational spectrum of 2-aminooxazole, a key prebiotic molecule in the RNA world hypothesis

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2-aminooxazole (2AO) is a key molecule in the prebiotic synthesis of RNA precursors and has important implications for the RNA World hypothesis and astrochemistry. Recent studies have shown that 2AO can be produced from small molecules like cyanamide and glycolaldehyde, which are present in interstellar space [1, 2, 3]

Three different spectrometers were used to provide precise experimental frequencies of 2AO in a broad frequency range for astrophysical use. The room-temperature rotational spectra in the 75–110 and 204–328 GHz regions were recorded using the Valladolid and Prague millimetre wave spectrometers [4, 5], respectively. Additional measurements in the 6–12 GHz frequency range were undertaken under conditions of supersonic expansion employing a broadband CP-FTMW spectrometer [6]. The molecule exhibits large amplitude motion of the amino group which results in a double-minimum potential function. Precise spectroscopic parameters are presented for the associated pair of states in the ground state as well as in some excited vibrational states.

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Exploring the rotational spectra of cyclopentylimine: insights from high-resolution millimeter wave spectroscopy

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Imines, organic compounds characterized by the presence of a carbon-nitrogen double bond, have garnered significant interest due to their potential role in the chemistry of the interstellar medium (ISM) and their relevance to prebiotic chemistry. The study of imines, therefore, not only helps in understanding the chemical diversity of the ISM but also provides insights into the pathways leading to the synthesis of prebiotic molecules.

This work represents the pioneer study of rotational spectra of cyclopentylimine. The spectra were measured in two frequency ranges from 204 to 240 and 293 to 328 GHz using the Prague millimetre wave spectrometer [1]. The results for the ground state and several excited vibrational states up to 500 cm^{-1} are presented together with the vibrational dependence of rotational and centrifugal distortion constants.

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A complete *ab initio* spectroscopic dataset of the hydrogen molecule for astrophysical studies

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Diatomic hydrogen is the simplest, yet the most abundant molecule in the Universe. Both H_2 and HD are present in the atmospheres of the giant planets in the Solar System [1], brown dwarfs [3], and interstellar medium [1].

The collisions of the molecules can be directly linked to their spectroscopic properties through the shape of an optical resonance. Our methodology steps beyond the conventional Voigt profile, taking into account the influence of speed-dependent broadening, shift, and velocity-changing collisions on the spectral lines. As will be demonstrated, consideration of such effects allows us to achieve subpercent accuracy when comparing with experiment [5, 5].

This presentation encapsulates our recent endeavors aimed at generating a complete spectroscopic dataset for accurate modeling of H_2 and HD interactions within diverse collisional environments. We report over 30 000 unique transitions, providing their positions, frequencies, pressure broadening and shift along with their speed dependencies as well as both the real and imaginary part of the complex Dicke parameter. We report the wide-range temperature dependencies of these parameters in the HITRAN double-power-law (DPL) format at temperatures from 20 to 1000 K [6].

The comprehensive dataset is based on ultra-accurate *ab initio* quantum-scattering calculations and involves H_2-He, HD-He, H_2-H_2, and HD-H_2 systems. Not only does it include electric dipole and quadrupole lines, but also magnetic dipole transitions for both H_2 and HD.

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Semi-classical calculations of line-broadening coefficients for C_2H_4 perturbed by N_2: analysis of hypotheses and technical details

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Molecular spectroscopy uses complex physical and mathematical models to determine important parameters of gas mixtures (concentration, temperature, etc.). However, besides some initial hypotheses, their numerical implementation requires multiple tests of truncation and convergence. Finally, these models need to be validated by verifying that their results are consistent with the existing experimental data.

Semi-classical calculations of room-temperature broadening coefficients in the ν_7 band of ethylene perturbed by nitrogen have been carried out on the basis of the Robert-Bonamy formalism [1] generalized to the case of asymmetric tops [2]. Besides the common classical-path approximation and other simplifying hypotheses, different approaches are available in the literature for this method to perform the bath-average of the line-broadening and line-shift coefficients [1, 3] which influence significantly the speed and quality of calculations. The calculation process involves also a series of necessary manipulations including numerical integration and handling infinite series. Careful verification of the convergence is necessary after the 'cuts' to guarantee the quality of the results.

In the present work, multiple convergence tests (radial potential components, intermolecular distances, resonance parameter, etc.) are considered. The influence of the simplified "symmetric top" approach is also analyzed. Finally, although the dense and complex experimental spectra make it difficult to establish experimental J and K_a dependencies, theoretical results provide a better understanding of the experiment.

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High resolution rotational and rovibrational spectroscopy of H_2CCCH^+

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In this presentation we review the rovibrational and rotational spectroscopic work on the propargyl H_2CCCH^+ cation done in the Cologne laboratories, applying the leak-out-spectroscopy (LOS [1]) method in a 4 K ion trapping apparatus. In an initial study, we measured the high resolution IR spectrum of the parallel ν_1 and $\nu_3 + \nu_5$ bands [2], allowing to predict rotational transitions in the vibrational ground state. Fourteen rotational lines of this ion were subsequently measured, leading, in the end, to the discovery of H_2CCCH^+ in the TMC-1 cloud [3]. However, given the nature of the studied transitions (all of them a-type), it was not possible to do an accurate determination of the A_0 rotational constant. In our latest work, we have studied vibration-rotation transitions in two perpendicular (b-type) bands: the fundamental ν_6 (antisymmetric H–C–H stretch) and the combination band $\nu_3 + \nu_7$ (C≡C stretch and CH_2 rock), in the 3056 - 3137 cm^{-1} region. The analysis of these transitions results in a seventy-fold improvement of the precision of the A_0 rotational constant of H_2CCCH^+.

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Systematic studies on the leak-out spectroscopy (LOS) technique in cryogenic ion traps

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Leak-Out spectroscopy (LOS) has proven to be a versatile tool in ro-vibrational and pure rotational spectroscopy of cold trapped ions [1, 2, 3]. The method relies on the transfer of vibrational to translational energy (V-T transfer) in collisions of the ions with neutral gas-phase atoms or molecules. Through this addition of kinetic energy, ΔE_{kin}, some ions overcome the barrier of the trapping potential, ΔE_{pot}, and are thus guided to the detector. The principle of LOS relies on the simple relation $\Delta E_{kin} > \Delta E_{pot} > E_{kin}$, where $E_{kin} \approx \mathrm{kT}_{ion}$ is the kinetic energy of the non-excited ions in the direction of the barrier. Thus it shall work best the larger ΔE_{kin} and the smaller E_{kin} while ΔE_{pot} shall be adjusted accordingly.

In practice, several experimental factors influence the sensitivity of LOS, e.g., the distribution of the kinetic energy of the ions, given approximately by the trap wall temperature T_{trap}, the barrier height, ΔE_{pot}, which is given by the voltage difference between the trap float and the exit electrode, the amplitude of the radio-frequency voltage responsible for the electrodynamical trapping in radial direction and the number density of the collision partner but also its mass to name the most obvious experimental parameters.

We report our experimental findings when varying some of these factors and interpret the results, e.g., with the aid of a semi-quantitative kinetics model which includes the V-T transfer process but also subsequent cooling collisions as well as the absorption and emission of photons. It is the aim of this study to gain a better, quantitative understanding of the fundamental physical processes happening inside the cold trap and to further improve LOS.

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High-resolution rovibrational and rotational spectroscopy of CCN$^+$

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The triatomic CNC$^+$ and CCN$^+$ molecular ions are thought to play important roles in the astrochemistry of interstellar clouds. While the high-resolution infrared spectrum of the non-polar ground-state CNC$^+$ isomer has been known for more than 30 years [1] no high-resolution spectrum of metastable CCN$^+$ had been reported yet. This work presents the first observation of the ν_1 'anti-symmetric' stretching mode of CCN$^+$ at 5 μm in an ion-trap apparatus using leak-out spectroscopy, LOS [2], and a quantum-cascade laser. This approach permitted an uncontaminated and artifact-free view on the rotation-vibration spectrum from $P(18)$ to $R(23)$. Subsequently, using an IR-mmW double resonance scheme [3] the pure rotational spectrum of CCN$^+$ was measured in the frequency range from 82 to 375 GHz. These measurements will enable the first radio-astronomical search for the investigated CCN$^+$ ion.

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Rotational spectroscopy of explosive taggants: study of 2,3-dimethyl 2,3-dinitrobutane

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The detection and characterization of explosives and their taggants, or of their degradation products, is a topic of crucial importance for public safety. It undoubtedly plays a key role in luggage screening and bombing scene investigations. At least two challenges need to be addressed by high-resolution spectroscopic techniques: the detection limit should be better than 1 ppb and the discriminating power should allow to unambiguously identify chemical species despite of similar properties [1]. The direct detection of classical explosives is out of reach for most spectroscopic techniques due to their extremely low vapor pressure at room temperature. Alternatively, they can be applied to the detection of explosive taggants which are intentionally added to explosives [2] or found as impurities because of the manufacturing process.

We present here the study of 2,3-dimethyl 2,3-dinitrobutane (DMDNB), a detection taggant largely used for plastic explosives. The microwave spectrum (2-20 GHz) was recorded with a free jet Fabry-Perot Fourier-transform microwave (FP-FTMW) spectrometer, which analysis was carried out with the support of quantum chemistry calculations. The spectroscopic parameters determined for the most stable gas phase conformation include the effective quadrupole coupling constants describing the hyperfine structure arising from the two ^{14}N nuclei. The progress of the development of a cavity-based mmwave spectrometer (150-215 GHz), the objective of which is to detect trace explosive markers, is also presented.[9]

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Vibrational spectroscopy of primary aliphatic amines

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Our current research focuses on analysis of vibrational bands structure of various butylamine isomers (*n*-butylamine, *sec*-butylamine and *tert*-butylamine). The absorption spectra were recorded by FTIR spectrometer Nicolet iS50 in a range 400-4000 cm^{-1} with a resolution of 0,25 $^{-1}$. These molecules represent asymmetric rotors which differ in their structure. In addition to that, they have 42 normal modes. It results in a highly complex structure of vibrational bands. Some earlier attempts to analyse vibrational spectra of *n*- and *tert*-butylamines can be found in literature [1, 2, 3]. However, the published analysis did not provide a complete picture. In our contribution, the assignment of spectral features is based on *ab initio* calculations. The Moller-Plesset 2 (MP2) method was utilized in connection with the correlation consistent valence double zeta (cc-VDZ) basis set. Anharmonic corrections were computed using analytic second derivatives, as implemented in the Gaussian16 program package. The dependence of vibrational energies on inversion movements was also investigated. Aminobutanes contain an amino group NH_2, with two hydrogen atoms capable of undergoing inversion above or below the symmetry plane. This movement creates a double-well potential. The vibrational wavefunctions in these two wells influence each other through tunnelling effects, resulting in shifting or splitting the vibrational energy levels.

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Ultrasensitive cavity ring-down spectroscopy at 1.39 μm

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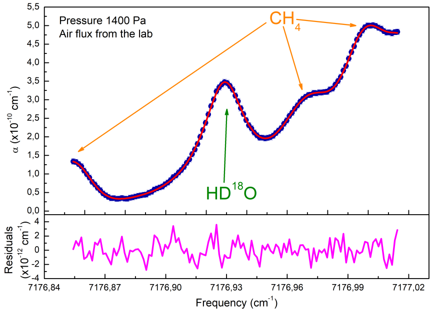
We report on the development, characterization, and test of a comb-locked cavity ring-down spectrometer (CL-CRDS) operating in the spectral region between 7120 and 7240 cm^{-1}. It represents an upgraded version of the setup described in Ref. [1].

The use of a new high-finesse optical resonator, showing an empty-cavity ring-down time of about 285 μs, allowed us to reach a minimum detectable absorption coefficient of 2×10^{-12} cm^{-1} for an integration time of about 40 s. This latter, inferred from an Allan-Werle analysis performed at a fixed laser frequency, was limited by mechanical, acoustic and thermal noises. Taking advantage of the frequency stability guaranteed by the comb, we performed spectra averaging over several days, thus removing efficiently baseline fluctuations from the absorption spectra. As a result, we could obtain a minimum detectable absorption coefficient of 3.7×10^{-13} cm^{-1}, which corresponds to a limit of detection for H_2O in N_2 of a few parts per trillion. The achieved sensitivity paves the way to the detection of extremely weak transitions, having intensities smaller than 10^{-30} cm/molecule. The figure here below reports an example of $HD^{18}O$ detection in ambient air.



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Disentangling the spectra of complex organic radicals using Faraday-rotation-based millimeter-wave instrumentation.

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Large radicals are involved in the formation and destruction processes leading to the formation of complex organic molecules (COMs) detected in the interstellar medium [1]. They are also important intermediates in atmospheric and combustion chemistry [2].

In this poster, a methodology to study specific dehydrogenated COMs in the gas phase will be described, illustrated by our recent results concerning the acetonyl (CH_3COCH_2), the methoxymethyl (CH_3OCH_2), and the methoxycarbonyl (CH_3OCO) radicals at millimeter and sub-millimeter wavelengths (160–450 GHz). The acquisition of the radical species spectra is performed using Faraday rotation modulation spectroscopy, allowing to detect paramagnetic species only and to discriminate the spin rotation components for each transition [3]. Thanks to the very broad spectral ranges covered in our recordings, we could rapidly identify series of lines using Loomis-Wood graphical representation [4], simplifying considerably the laboratory detection of these new species for which no rotational information was available in the literature.

We will present the instrumental developments and the methodology used to analyze these relatively large heavy radicals. This methodology will be applied to many other large radical species in the future.

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Hydrogen bonding in paraxanthine-water complexes: an *ab initio* approach

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Paraxanthine, a caffeine derivative found in chocolate, tea leaves, and other sources, has garnered significant scientific and clinical interest due to its potential biological and pharmacological applications. As a heterocyclic molecule, paraxanthine possesses multiple sites that can act as hydrogen bond (H-bond) donors or acceptors when interacting with other biological molecules. To understand these interactions at a fundamental level, this study explores the 1:1 complexes formed between paraxanthine and water molecule. We have employed MP2 and wB97XD calculations with a 6-311 ++G(d,p) basis set to investigate the electrostatic potential energy surface of these complexes. An extensive search has yielded various 1:1 paraxanthine-water structures involving O-H—O, N-H—O, O-H—N, and C-H—O H-bond interactions. Notably, all stable structures exhibited dual H-bonding, with the complex featuring O-H—O and N-H—O interactions identified as the global minimum. Conversely, the structure with the C-H—O interaction is the least stable. To further elucidate the stability of these complexes, natural bond orbital (NBO) analysis is performed to reveal the role of hyperconjugation interaction. Additionally, the charge density topology of each complex is analyzed using Atoms in molecule (AIM) calculations.

A hybrid approach to generating diatomic line lists for high-resolution studies of exoplanets and other hot astronomical objects: updates to ExoMol MgO, TiO and VO line lists

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The best molecular line lists for astrophysical applications are able to provide high-accuracy line positions and a complete set of transitions. The former is required to facilitate molecular detections in exoplanets using techniques like high-resolution cross-correlation spectroscopy, while completeness is needed for the accurate determination of spectroscopic and thermodynamic properties. The use of empirical energy levels determined by the Marvel [1] procedure is a standard way to improve accuracy. This work presents methods to extend this framework using machine-learned corrections (predicted shifts) and extrapolations to isotopically substituted species. Use of energies generated with other techniques such as effective Hamiltonian calculations are outlined. These methods are used to update ExoMol [2] line lists for the primary MgO, TiO, and VO species, as well as for several important isotopologues [3, 4]. This has enabled the greater provision of high-accuracy data and successful detections in stellar and exoplanetary atmospheres [5, 6].

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Collisional broadening of the O_2 sub-THz rotational lines

M. A. Koshelev*[1] *, I. N. Vilkov*[1] *, G. Yu. Golubyatnikov*[1] *, A. Yu. Sekacheva*[1] *,
***D. S. Makarov*[1] *, M. Yu. Tretyakov*[1]**

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Advances in techniques of the submillimeter wavelength range open up the possibility of their application to the remote sensing of the atmospheres and planetary surfaces, which in turn requires obtaining accurate laboratory measurements of the diagnostic spectral lines' parameters. In this study the profiles of the subteraherz rotational lines of the oxygen molecule broadened by pressure of nitrogen and oxygen were studied by means of the video spectrometer and a radioacoustic detection (RAD) spectrometer. As a result, the central frequencies of the transitions were refined and the coefficients of collisional broadening and central frequency shifting of the lines were determined. For the first time, the influence of the collision cross-section dependence of the absorbing molecule on its speed ('wind' effect) on the profiles of oxygen rotational lines has been studied. [10]

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[10] The study was supported by the Russian Science Foundation project 22-72-10118 (https://rscf.ru/en/project/22-72-10118/).

Free jet millimeter wave torsion-rotation spectrum of a silicon containing molecule: dimethylsylane

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The research and identification of molecular species in the interstellar medium relies heavily on spectroscopic techniques, such as microwave spectroscopy, due to the fact that the rotational spectrum of a molecule can be regarded as its fingerprint which allows a straigthforward and unambiguous determination.

In the interstellar and circumstellar medium, silicon can be found in form of silicates in the core of dust grains surrounding carbon stars; when the grains are destroyed it quickly reacts to form SiO and SiS. As today, among the 260 and more molecular species found in the interstellar medium less than fifteen are silicon-based, so the research of molecules containing silicon is crucial to build better theoretical models about formation and reaction pathways[1].

In the hope that dimethylsilane could be found in environments similar to those where most of the silicon-containing species have been found,[2] the measurement of its rotational spectrum was extended to higher frequencies.

The spectra of dimethysilane and its isotopologues in the frequency interval 60 and 78 GHz were measured in a supersonic expansion, assigning the transitions belonging to four isotopologues, the ones containing the isotopes ^{28}Si, ^{29}Si, ^{30}Si and ^{13}C. Dimethylsilane exhibits internal rotation of the two methyl groups around their own axes, which has the effect of splitting every rotational transition in four components with different intensity, labelled AA, EE, EA and AE according to the symmetry of the torsional wavefunctions.

At the conclusion of the experiment we successfully characterized the spectra of the four species in exam, obtaining their spectroscopic parameters, conducted a geometry analysis and built a predictive model, that of the internal rotation splitting, useful for the research of these molecule in the interstellar medium in different conditions.

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Monitoring of the synthesis and temporal evolution of tritiated methane mixtures by Raman spectroscopy

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Tritium, the radioactive isotope of hydrogen, is an indispensable reagent for future tokamak-type nuclear fusion reactors (like the International Thermonuclear Experimental Reactor, ITER). It also is the key component for the Karlsruhe Tritium Neutrino mass experiment (KATRIN) at the TLK of the Karlsruhe Institute of Technology, which aims to obtain neutrino masses with higher precision. Using tritium in large quantities, radiochemical reactions take place during their circulation through the system, leading to molecular products, such as water isotopologues, Q_2O, and tritiated methane species, CQ_4 normally accumulating in low concentration (where Q can be protium (H), deuterium (D) and tritium (T).

Raman spectroscopy has become an essential analytical tool for the in-line monitoring of these gaseous mixtures. However, spectroscopic knowledge of tritiated methanes is rather incomplete, due to the very low concentrations used in the investigations to date. For the results presented here the CQ_4 compounds were synthesised in large quantities using a stepwise enrichment procedure based on catalytic isotope exchange reactions to increase the concentrations to more than 20 The resulting mixtures were composed of the family $CT_xH_{(4-x)}$, as well as the hydrogen molecular isotopologues H_2, T_2 and HT. The composition of the samples has been evaluated by depolarisation Raman spectroscopy, allowing the semi-quantification through the $\nu_1(Q_1)$ bands of the different species of the isotope-substituted methane family.

The spectroscopic data also reveal that the composition of the samples evolve over time. Complementary mass spectrometry measurements showed that several of the observed Raman signals correspond to molecules of up to 5 carbon atoms. Our preliminary analysis indicates that the radiochemical processes produce tritiated hydrocarbons with a predominance of fully tritiated ethylene.

Recent advances on carbon disulfide molecular clusters: discovery and characterisation of new isomers

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In this contribution we present some of our latest experimental and computational results on molecular clusters involving carbon disulfide, CS_2. For the pure trimers, $(CS_2)_3$, the calculations assisted in the characterization of a new isomer (having C_2 symmetry) whose IR bands were detected and analyzed in the regions of the ν_3 and $\nu_1 + \nu_3$ bands of CS_2. In the case of mixed dimers involving one unit of water, CS_2-H_2O, our *ab initio* calculations led to identify three stable minima instead of the two previously reported. Here we report the first rotationally-resolved infrared spectra of a new $(CS_2)_3$ trimer and of the two most stable isomers of the CS_2-H_2O dimer, together with their accurate spectroscopic analysis and thorough investigation by experimental and computational methods.

Improved Hamiltonian model for axially symmetric C_{3v} molecules: precise ro-vibrational analysis of the ground state and the ν_2/ν_4 diad of AsH_3

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The effective Hamiltonian of the axially symmetric C_{3v} molecule was modified and improved in comparison with the models known in the literature. On that basis, the ro-vibrational structure of the ν_2/ν_4 diad of the AsH_3 molecule was re-analyzed. The high resolution spectra were recorded with the Bruker IFS 125HR spectrometer in Braunschweig, Germany, and analysed. More than 5000 transitions (which is more than two times higher in comparison with the data known in the modern literature) with the maximum values of quantum numbers $J = 28$ and $K = 28$ (for comparison, $J^{max} = 21$ and $K^{max} = 20$ are known in the literature) were assigned in the experimental spectra and theoretically described with the derived Hamiltonian model with the d_{rms} better than 7×10^{-5} cm^{-1}. The ground state parameters were improved by the use of a set of more than 3000 ground state combination differences ($\Delta J = 0, 1, 2$; $\Delta K \leq 15$; $J^{max} = 28$; $K^{max} = 28$). Ground state parameters are obtained from the weighted fit, which reproduce the initial ground state difference values with the $d_{rms} = 4.7 \times 10^{-5}$ cm^{-1} (for comparison, the best sets of the ground state parameters known in the literature reproduce the same initial ground state combination differences with an accuracy about 30 times worse). Exotic a_1/a_2 splitting for the states with the values of the quantum number K up to 16 are experimentally recorded and theoretically described.
[11]

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[11] The study was partially supported by the CSU NMNT TPU, Russia (RF MES project #075-15-2021-710).

Implementation of a two-color-REMPI scheme for molecular beam studies

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In organic chemistry and biology molecular chirality is omnipresent and an extensively studied topic. In contrast, using purely physical methods to investigate chirality is rather sparse. In particular, the usage of light for the identification and control of chirality on a molecular level constitutes fundamental challenges. Aspects of these challenges are the distinction between enantiomers, enantiomer switching, and enantio-selective state preparation, which demand the development of precision spectroscopic tools and techniques. Our vision is to use a combination of microwave and infrared radiation to enable enantiomeric selectivity.

Here we present progress in the development of a spectrometer to study chiral species in a molecular beam that can be selectively excited and detected in a time-of-flight mass spectrometer using resonance-enhanced multiphoton ionization (REMPI). Our current investigations are focused on testing different UV and optical wavelengths in a two-color pump probe setup to improve the spectral selectivity and spectral range of the spectrometer with respect to possible ionization schemes using nanosecond and picosecond laser systems. Manipulation and state preparation techniques that can be used to study chiral molecules will be discussed, and test results for different non-chiral samples will be presented.

Deperturbation analysis of the $A^1\Pi$ $(v = 4)$ level in CO based on the VUV and Vis-FT-spectroscopies

***S. Ryzner*[1] *, A. Stasik*[1] *, W. Szajna*[1] *, R. Hakalla*[1] *, M. I. Malicka*[2] *, R. W. Field*[3] *, N. De Oliveira*[4] *, W. Ubachs*[5]**

[1]Institute of Physics, University of Rzeszów (Poland), [2]The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology (Poland), [3]Department of Chemistry, Massachusetts Institute of Technology, Cambridge (USA), [4]Synchrotron SOLEIL, Orme de Merisiers, St. Aubin (France), [5]epartment of Physics and Astronomy, Vrije Universiteit, Amsterdam (Netherland)

We would like to present the first deperturbation analysis of the $A^1\Pi$ (v=4) level in the $^{13}C^{18}O$ molecule. It was performed based on the spectra obtained using two complementary FT methods: *(i)* the emission spectroscopy in the VIS region (Bruker IFS-125HR spectrometer; University of Rzeszów, Poland) and *(ii)* the VUV absorption spectroscopy by means of the wave-front-division spectrometer working as the end station on the DESIRS beamline (SOLEIL synchrotron, St. Aubin, France).

The deperturbation analysis of the $A^1\Pi(v = 4)$level was carried out using the PGOPHER programm Ref. [1]. An effective Hamiltonian and the term-value fitting approach were applied. As a result, precise molecular parameters of the $^{13}C^{18}O$ levels were obtained, including: molecular constants, interaction parameters as well as ro-vibronic terms of the $A^1\Pi(v = 4)$ level and its perturbers.

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]–[7].

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Invited Speaker WA

Wednesday, September 4, 9:00
Chair: A. Lesarri
Room B

Quantitative analysis of isotope mixtures for applications in pharmaceutical chemistry using broadband rotational spectroscopy

B. Pate[1]

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Isotopically labeled compounds have long played a role in pharmaceutical chemistry to understand how the active pharmaceutical ingredient (API) is metabolized. Recently, there has been increased interest in using deuterium labelling directly in the drug design process. When deuterium is substituted at a metabolic weak point in the API, the kinetic isotope effect reduces the metabolism rate. This isotopic exchange can lead to a medicine that has higher efficacy and safety. The recent approval of deuterated drugs has spurred interest in precision deuteration chemistry where the isotopic substitution is made at a single position in the molecule and with high yield. These reactions make it possible to create complex deuteration patterns with low amounts of isotopic impurities from over-deuteration, under-deuteration and mis-deuteration. The characterization of the reaction products from precision deuteration methods poses several challenges to existing analytical chemistry methods like mass spectrometry and NMR spectroscopy. Molecular rotational spectroscopy is ideally suited to the analysis of mixtures of isotopic species because each chemically distinct isotopic variant has a unique spectral signature. Furthermore, the spectral patterns of different isotopic variants can be predicted to high accuracy using quantum chemistry and the resolution of pulsed-jet, Fourier transform microwave spectrometers makes it possible to analyze complex mixtures with negligible spectral overlap. Recent examples of rotational spectroscopy analysis of deuterated compounds will be presented including cases where analysis of isotopically chiral molecules is needed to assess the performance of the precision deuteration reaction.

How increased use of remote sensing technique for monitoring the health of our environment translates to additional requirements as to molecular spectroscopy databases

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Monitoring environmental parameters such as vegetation and crop health, land use changes, air pollutants, and greenhouse gas emissions using remote sensing techniques has become routine. These techniques are essential for supporting measures to *green* our economic activities and for verifying the impact of these measures.

Many remote sensing techniques, whether space-, air-, or ground-based, use spectrometric methods that require traceable spectroscopic data. This presentation focuses on using infrared spectrometry in remote sensing to monitor air quality and climate pollutants in the atmosphere. There is growing interest in urban and industrial emissions and in trace gases that have previously gone undetected or whose importance was underestimated or misunderstood. Also, advances in observational technologies and the increasing demand for accuracy and precision in observations require ever higher-quality spectroscopic data.

We will illustrate these points with examples from recent and ongoing research projects related to air quality and climate change. These examples highlight the current challenges in meeting the spectroscopic data requirements. The goal of this presentation, particularly the specific examples, is to foster enhanced collaboration with the spectroscopy community to address these needs.

Contributed speaker WB1
Wednesday 4 September, 11:00
Chair: S. Yurchenko
Room B
Atmospheres

Oxidation product analysis of an α-pinene discharge by microwave spectroscopy

J. R. Moran[1] ***, A. L. Steber***[1] ***, I. Peña***[1] ***, C. Cabezas***[2]

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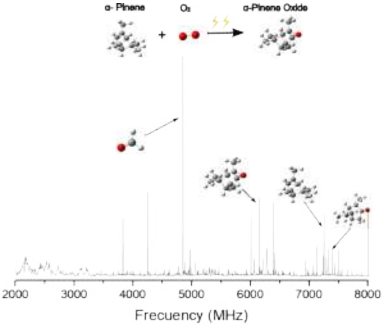
Monoterpenes are biogenic organic volatile compounds (BVOCs) emitted into the atmosphere from vegetation. Amongst them, α-pinene ($C_{10}H_{16}$) is ubiquitous and is often observed to have the highest emission rates in the troposphere. Its photo-oxidation leads to a variety of monoterpenoids with lower vapor pressures that may participate in the formation of secondary organic aerosols (SOA). The formation of SOA using α-pinene as precursor has been the subject of numerous studies. However, the mechanisms of oxidation in the atmosphere are complex and far from being completely understood. Here, using chirped-pulse Fourier transform microwave spectroscopy, new assignment tools, and databases of computed structures, the discharge products of α-pinene in combination with molecular oxygen have been characterized in the 2 to 8 GHz frequency range. Among the oxygenated species observed, α-pinene oxide [1] has been identified in our experiment, thus continuing to highlight the use of electrical discharge sources as a valuable tool to generate oxidation products of atmospheric relevance.



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N_2 and O_2-broadening coefficients of CH_3Br ro-vibrational lines in the ν_2 and ν_5 bands

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Methyl bromide CH_3Br has been identified as the major contributor to the overall stock of atmospheric bromine [1]. Due to the strong ozone depletion capability of the activated bromine species, the total atmospheric bromine load needs to be carefully monitored. It would therefore be interesting to follow the evolution of its concentration in the atmosphere wich requires high-precision data on collisional broadening by the principal atmospheric species, particularly by molecular nitrogen and oxygen (N_2 and O_2). In this work, foreign gas effects were measured for the rovibrational lines of CH_3Br in the ν_2 and ν_5 fundamental bands perturbed by N_2 and O_2. The measurements were made by analyzing 12 laboratory absorption spectra for each perturber recorded at room temperature (295K). The spectra were recorded at high resolution (0.005, 0.003 or 0.002 cm^{-1}) using the Fourier transform spectrometer Bruker IF125HR located at the LISA facility in Creteil equipped with a cell with an optical path of 0.849 m. We have been able to determine the N_2 and O_2-broadening coefficients of over 600 transitions in each of the ν_2 and ν_5 bands with quantum numbers up to J= 49 and K = 10.The measured N_2-broadening coefficients range is from 0.0737 to 0.1284 cm^{-1} atm^{-1}; for O_2 these coefficients vary from 0.0597 to 0.1057 $cm^{-1} atm^{-1}$. Comparisons between measurements in the two bands of CH_3Br did not show any clear vibrational dependence. The J and K dependences of the N_2- and O_2-broadening coefficients have been observed and modeled.

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Sub-mm line shape analysis of methyl bromide (CH_3Br)

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CH_3Br plays an important in the earth's atmosphere. The naturally and anthropologically emitted alkyl halide is capable of depleting ozone in the atmosphere. Its environmental importance induced bans in its applications, and requires a close monitoring of its atmospheric concentration. Numerous studies have been dedicated to ro-vibrational analysis of CH_3Br in the infrared and THz spectral bands, as well as intensities, positions and broadening parameters in the infrared region [1, 2]. However, line profile analysis remains lacking in the THz domain. Within this context and to determine the broadening parameters of CH_3Br for environmental applications, we present herein the determination of line positions, intensities, and self, N_2 and O_2-broadening coefficients of CH^{79}_3Br and CH^{81}_3Br isotopologues. The experimental coefficients were measured based on spectra recorded at different pressures ranging from 0.1 to 1 mbar. A multi-spectra multi-line fitting algorithm was used to fit amplitude and frequency-modulated absorption spectra, recorded using frequency multiplication spectrometers in the 70 GHz-1.1 THz range.

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Isotopologue extrapolation of energy levels for polyatomic molecules: rotation-vibration energies of ammonia $^{15}NH_3$

O. A. Smola[1] **,** ***S. N. Yurchenko***[1] **,** ***J. Tennyson***[1]

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It is common in variatonal calculations of rotation-vibrational energies of isotopologues polyatomic molecules to use the same (Born-Oppenheimer) potential energy surface (PES) for different isotopologues. However the associated errors from neglecting the mass-dependent, non-adiabatic contributions can be significant. An empirical isotopologue extrapolation approach has been proposed to mitigate such systematic effects [1]. The method of isotopologue extrapolation of energies assumes that the residual between the experimental and calculated value of a given ro-vibrational level (obs.-calc.) computed using an *ab initio* PES remains approximately unchanged upon isotopic substitution. Under this assumption, the residual obs.-calc. between empirical and *ab initio* energies of a reference isotopologue can be added to the corresponding *ab initio* energies of isotopically substituted species to form isotopologue extrapolated (IE) energies. We explore the application of this approach for $^{15}NH_3$, where IE levels are derived from the MARVEL energies for $^{14}NH_3$ [2] using the *ab initio* PES computed by [3]. We find that the accuracy of IE energies displays a greater band centre dependence than in the previous work [1]. Despite this, there are still a number of bands for which the IE levels are more accurate than those variationally computed using a refined PES of $^{15}NH_3$. In total, we generate 326 IE ro-vibrational levels of $^{15}NH_3$ and use them to improve the accuracy of our new CoYuTe-15 line list for this molecule [4].

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Line positions and intensities of the $\nu_3 + \nu_6$ band of methyl fluoride

H. Ziadi[1], ***M. Rey***[2], ***B. Grouiez***[2], ***M. Rotger***[2], ***A. V. Nikitin***[3], ***H. Aroui***[4]

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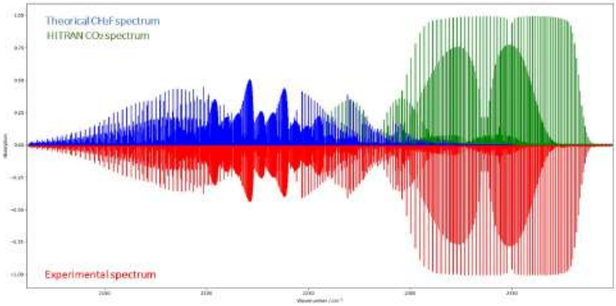
Methyl fluoride CH_3F being a minor molecular constituent of the Venus atmosphere [1], is also present in the earth atmosphere at low concentration. Infrared spectra of $^{12}CH_3F$ were recorded in the 2200 cm^{-1} region using a Fourier transform spectrometer in Reims, France, with a resolution of 0.003 cm^{-1}. The measurements were conducted using a White-type cell with a path length of 8.26 m filled with 1 mbar of CH_3F. This spectral region corresponds to the $\nu_3 + \nu_6$ band, which had not been observed previously. Experimental line positions and intensities were determined using the Voigt line shape as a model in multispectral fitting and analyzed using the effective Hamiltonian and the effective dipole moment, expressed in terms of irreducible tensor operators adapted to symmetric top molecules (C_{3v}). The band assignment was carried out up to $J = 45$ and $K_a = 15$. Over 3100 lines were assigned, with 2500 line positions fitted to achieve an RMS of 7.4589×10^{-4} using 18 molecular parameters. Initially, more than 400 line intensities of isolated transitions were fitted with an RMS of 1.3219×10^{-1} using 6 terms of the dipole moment expansion.



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High-resolution spectroscopy of protonated diacetylene, $H_2C_4H^+$

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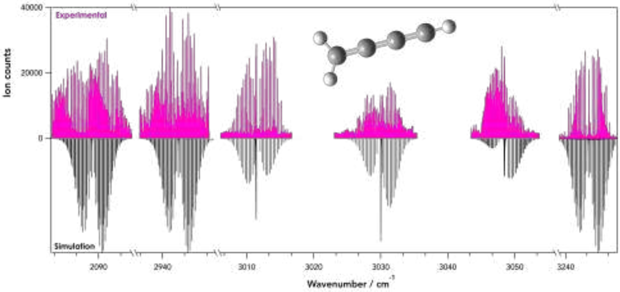
Unsaturated hydrocarbons with a linear carbon backbone are important constituents of the interstellar medium (ISM), many of which have been detected in the ISM and hydrocarbon-rich planetary atmospheres. Recently, $H_2C_3H^+$ was detected towards the cold molecular cloud TMC-1 [1]. Ion-neutral reactions in these cold environments can play an important role in the bottom-up approach towards cyclic and polycyclic aromatic hydrocarbons.

In this work, the first high-resolution rovibrational spectrum of protonated diacetylene ($H_2C_4H^+$) will be presented using the recently developed leak-out spectroscopy method [2]. The combined use of a QCL and a cw-OPO allowed recording the fundamental acetylenic C–C stretch, the acetylenic C–H stretch, as well as the symmetric and anti-symmetric CH_2 stretches along with additional combination bands with two cryogenic 22-pole ion trap setups available in Cologne. The rotational constants for the ground state and the four vibrational states will be presented, which could aid future astronomical searches for this hydrocarbon ion.



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Overtone transition $2\nu_1$ of HCO^+ and HOC^+ — origin, radiative lifetime, collisional quenching

M. Jiménez-Redondo[1] , **P. Caselli**[1] , **P. Jusko**[1] , **L. Uvarova**[2] , **M. Kassayová**[2] , **P. Dohnal**[2]

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The formyl cation, HCO^+, and its 1.7 eV higher energy isomer isoformyl cation, HOC^+, are one of the most simple isomeric systems. HCO^+, probably the second most important cation in space after $H_3{}^+$, was interestingly first detected under the name “X-ogen”, prior to its laboratory identification in the ’70s. Surprisingly the higher isoformyl cation isomer, HOC^+, was identified in the lab and in space only about a decade later. We identify the first overtone vibration transition of C–H/ O–H stretch ($2\nu_1$) in HCO^+ and HOC^+, using a laser induced reaction action scheme inside a cryogenic 22 pole radio frequency ion trap [1]. We explore the sensitivity of the trapping potential to m/z (mass/charge) ratio in order to introduce time defined m/z ejection of particles from the trap, i. e., allowing us to record a background free action spectra. We located the band origins at 6078.68411(19) and 6360.17630(26) cm^{-1}, for HCO^+ and HOC^+, respectively. We estimate the radiative lifetime and the quenching rate of the trapped ion in the $2\nu_1$ state by varying the number density of the neutral action scheme reactant (CO_2 for HCO^+, Ar for HOC^+) and collisional (quenching) partner reactant inside the ion trap (He, H_2, N_2).

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Contributed speaker WC1

Wednesday 4 September, 11:00
Chair: S. Schlemmer
Room C
Precision spectroscopy

Precision spectroscopy of tritiated molecules

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Over the past decades, precision spectroscopy has emerged as a key technology in various fields, including (i) tracing and monitoring molecules in the atmosphere, (ii) analyzing astrophysical processes, and (iii) testing theories of the simplest systems. However, tritium and tritium-containing molecules, the radioactive isotope of hydrogen, have not been adequately included in these fields. Recent work at the Tritium Laboratory Karlsruhe is addressing this gap by precisely measuring ro-vibrational transitions in molecular tritium and tritiated water.

In this presentation, the overview of the results includes high-resolution FTIR spectroscopy of tritiated water species [1, 2], CARS spectroscopy of HT, DT, and T_2 [3], and NICE-OHMS spectroscopy of HT [4][12]. The significance and potential applications of these findings for astrophysics, environmental and process monitoring, and theoretical studies are discussed. The challenges for future precision spectroscopy of tritium and tritiated molecules are also highlighted.

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Precision measurements and tests of fundamental physics with cold molecules

A. Bonifacio[1] ***, M. Saffre***[1] ***, Y. Liu***[1] ***, N. Cahuzac***[1] ***, S. Tokunaga***[1] ***, A. Cournol***[1] ***,***
M. Gonçalves[1] ***, A. Kaladjian***[1] ***, E. Cantin***[1] ***, O. Lopez***[1] ***, A. Amy-Klein***[1] ***,***
M. Manceau[1] ***, B. Darquie***[1]

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High-precision spectroscopy of complex polyatomic molecules is crucial in various fields, from atmospheric and astrophysical studies, requiring accurate molecular parameters, to fundamental physics, for tests of fundamental symmetries and measurements of physical constants and their variations in space and time. At the Laboratoire de Physique des Lasers, we are developing a new ultra-high-precision mid-infrared (MIR) spectrometer to measure rovibrational frequencies of complex molecules with unprecedented accuracy, down to the 10^{-15} level for the most stringent fundamental physics tests. This spectrometer uses ultra-stable, SI-traceable quantum cascade lasers (QCLs) and a source of cold complex molecules.

Currently, a 10 μm QCL source is stabilized at a sub-Hz level against some of the world's best frequency standards using an ultra-stable signal transferred by optical fiber from the French metrology institute. It demonstrates record relative frequency stability better than 10^{-15} at 1s and a frequency uncertainty at the 10^{-14} level or below [1]. I will present work on extending our spectrometer tunability using cutting-edge, ultra-fast photonic MIR technologies such as a 60 GHz Quantum Well Infrared Photodetector (QWIP) and extending its spectral coverage to the 6 μm region [3].

In our setup, a gas of complex species is cooled to a few kelvin through collisions with a buffer gas in a cryogenic cell [4]. We are currently focusing on several types of complex molecules: (i) polycyclic aromatic hydrocarbons (PAHs), which are present in the atmosphere and interstellar gas clouds [5], (ii) complex organometallic compounds such as methyltrioxorhenium, which we have already buffer gas cooled [6], and its chiral derivatives as well as other chiral compounds like ruthenium(III)-tris-(acetylacetonato) [7]. These chiral molecules are promising for measuring the electroweak-interaction-induced tiny energy difference between enantiomers, a signature of parity violation [4].

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High (sub-10 mHz) resolution molecular spectroscopy in the mid-IR to THz range using broadband dual frequency comb method

K. Vodopyanov[1] ***, D. Konnov***[1] ***, Y.-C. Chan***[2] ***, E. L. Temelkova***[3] ***, A. Muraviev***[4] ***, D. Nesbitt***[5]

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The combination of broadband frequency combs obtained through intrapulse difference frequency generation from a femtosecond laser source and electro-optic sampling using few-optical-cycle probing pulses offers a novel technique for ultrasensitive high resolution molecular spectroscopy over an exceptionally broad mid-IR to THz range (6.6–200μm, 50-1500cm^{-1}) with referencing the frequency axis to a rubidium atomic clock. In this talk, we discuss first spectroscopic applications of this powerful technique, presenting preliminary data and analysis of high S/N Doppler limited molecular spectra in the mid IR frequency range for several species relevant to terrestrial and exoplanetary atmospheres. Specifically, we observe and identify c-type rovibrational bands of isoprene corresponding to out-of-plane methylenic bending in the 800-1200 cm^{-1} region, a/b/c-type methyl rocking rovibrational bands of dimethylsulfide (900-1100 cm^{-1}), as well as multiple hybrid a/b-type rovibrational bands in ethanol due to asymmetric CO/CC stretching and COH bending vibrations near 1000cm^{-1}. Of special interest, the THz frequency comb capabilities from intrapulse difference frequency generation also permit pure rotation-tunneling spectra to be observed, which can be used to selectively detect trace conformers with a non-vanishing dipole moment. As a demo, we demonstrated, for the first time to our knowledge, the simultaneous measurement of rovibrational (at 670-1000cm^{-1}) and rotational (at 85-120cm^{-1}) spectra of ammonia molecule. Progress toward using this novel capability to further characterize large amplitude C-C-C-C dynamics of room temperature gauche- and cis-1,3 butadiene conformers in the presence of excess trans-1,3 butadiene will be discussed.

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Unrivaled accuracy in measuring rotational transitions of greenhouse gases: THz-CRDS of CF_4

F. Simon[1], A. Cuisset[1], C. Elmaleh[1], F. Hindle[1], G. Mouret[1], M. Rey[2], C. Richard[3], V. Boudon[3]

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Tetrafluoromethane CF_4 is a very stable greenhouse gas, with an atmospheric lifetime of 50,000 years, and a high warming potential 6500 times that of CO_2. Over the last 15 years, its atmospheric concentration has increased at a rate of 0.8 ppt/year [2]. The accurate quantification of CF_4 is key to understanding the contribution of its emissions on the radiative forcing budget, the most precise spectroscopic parameters possible are hence required. In this study, a novel high finesse THz cavity, providing an interaction length in excess of 1 *km*, has enabled highly resolved spectra, and quantification of the weak transitions of CF_4 by Cavity Ring-Down Spectroscopy (CRDS) [3]. More than 50 pure rotational $P_6 - P_6 : \nu_3 - \nu_3$ lines of CF_4 have been measured, yielding both position and intensity with unequalled precision. Several tetrahedral splitting are fully resolved and measured with sub-MHz accuracy. Moreover, CRDS-THz allows determining absolute intensities and, using a global fit of the ν_2 polyad series, a CF_4 dipole parameter, namely $\tilde{\mu}_{3,3}$, has been fitted to $106.38(53)$ *mD*. This value is in a very good agreement with that of the *ab initio*-based parameter deduced from a dipole moment surface. A resulting line list composed of 25 863 transitions was used to model the whole CF_4 rotational spectrum and to update the TFMeCaSDa database [4] for future spectroscopic and monitoring activities.

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Symmetry aspects and tunneling splittings of the torsional energy levels of the hydroquinone molecule

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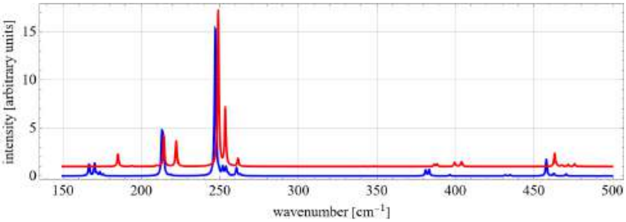
The hydroquinone (HDQ) molecule is the one of three dihydroxybenzenes having two hydroxyl groups in para-arrangement. Recently, the torsional IR spectra of the catechol [1] and resorcinol [2] molecules (two remain dihydroxybenzenes) were predicted. Although the last two molecules belong to C_{2V}(M) molecular symmetry group, HDQ molecule belongs to D_{3H}(M) molecular symmetry group. This fact has not yet to be reported in the literature to our knowledge. To predict torsional IR spectra of the trans- and cis- HDQ conformers the 2D potential energy surface, kinetic coefficients and components of the dipole moment surfaces were calculated at the MP2/CBS(D,T,Q) and CCSD(T)/dAug-cc-pVTZ levels of theory. Then we used the technics reported in [1, 2] to solve numerically vibrational Schrödinger equation of restricted dimensionality to find the values of the torsional energy levels as well as corresponding vibrational wave functions. Calculated torsional IR spectra of the trans- and cis-conformers as well as their mixture at the equilibrium conditions at the 300 K represented in Figure. The tunneling splittings of the ground states: 1.26×10^{-6} and 1.64×10^{-6} cm^{-1} for trans- and cis-conformers respectively were found at the MP2/CBS(D,T,Q) level of theory.



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Si-referenced HCOOH vibrational spectroscopy at the 20 Hz level

M. Leuliet[1] **, A. Mbardi**[1] **, B. Argence**[1] **, J.-Ph. Karr**[1] **, L. Hilico**[1]

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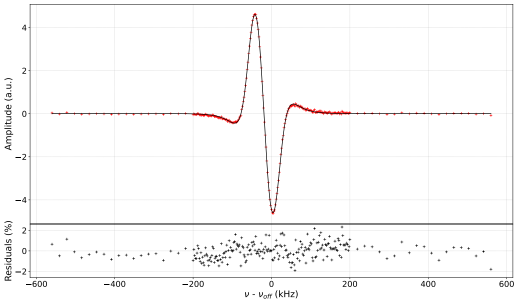
The proton-to-electron mass ratio is a fundamental constant that can be measured using high resolution spectroscopy of H_2^+ and QED calculations [1]. For this purpose, we have developped a *Système international*-referenced IR spectrometer at 1091 cm^{-1} using optical frequency synthesis at 32.7 THz.

We present (i) the spectrometer including a 1.5 μm comb optically locked to the REFIMEVE ultrastable signal, a CO_2 laser, a QCL, sum frequency mixing, beatnote detection and phase lock loops and (ii) the measurement campaign we have performed on the $J'{=}21, K'_a{=}2, K'_c{=}20 \leftarrow J''{=}21, K''_a{=}3, K''_c{=}19$ HCOOH, improving on previous results line [2].

The figure shows a saturated absorption line detected in third harmonic (pressure 1 μb, mod. freq. 220 Hz, mod. depth 45 kHz), the fit and the residuals. Analysis of more than 6000 such spectra for different pressures, modulation parameters and laser intensities allows extracting the central frequency at the sub ppt level and pressure broadening coefficient.



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A systematic reduction of the effective hamiltonians using normal ordering of cylindrical angular moment operators

I. M. Efremov[1] , ***S. V. Krasnoshchekov***[1] , ***D. V. Millionshchikov***[2]

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The conventional methodology for analysis of high-resolution molecular vib-rotation spectra is based on fitting parameters of effective Hamiltonians. Particular forms of such effective Hamiltonians are usually selected by trial-and-error procedures, comparing and analyzing their various forms.

As it is known from Watson's works [1, 2], the number of physically meaningful constants can be determined theoretically taking into account symmetry considerations and using a series of unitary rotational transformations (reductions) for cancellation of dependent parameters. The so-called *A*- and *S*-reductions up to octic terms can be derived analytically and are most commonly used for fitting molecular spectra of symmetric and asymmetric tops [2, 3]. As was noted by Watson, the lower symmetry groups (C_s, C_i, etc.) can be reduced to the standard orthorhombic case (C_{2v}, D_{2h}) by an additional rotational transformation, but its form is usually not considered explicitly.

The *ab initio* solution of the direct vibration-rotation problem using the Watson Hamiltonian can be achieved through numerical-analytic canonical perturbation theory in operator form [4]. This approach can be efficiently implemented using normal ordering of ladder operators of angular momentum (J_z, J_+, J_-) as it solves the problem of evaluation of rotational commutators. The developed theoretical approach and high-performance computer codes make it possible to calculate refined quartic constants in the fourth order, sextic and octic constants in the sixth order. Numerical examples demonstrating an efficiency of this approach are provided.

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Contributed speaker WD1

Wednesday 4 September, 11:00
Chair: M. Lepère
Room D
Laser spectroscopy

Exploring molecular orbitals and ionization dynamics in 2,3-difluoropyridine: insights from high-resolution VUV-MATI mass spectroscopy

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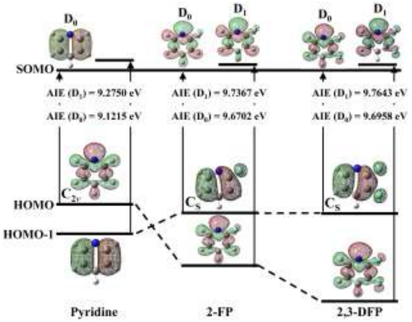
Pyridine dericatices play crucial roles in various scientific fields, with recent studies focusing on their molecular orbitals and electronic states. Here, we present an investigation into 2,3-difluoropyridine (2,3-DFP) using high-resolution vacuum ultraviolet mass-analyzed threshold ionization (VUV-MATI) spectroscopy and quantum chemical calculations. The ionization energy of 2,3-DFP was determined to be 78,202 ± 4 cm^{-1} (9.6958 ± 0.0005 eV) from the VUV-MATI spectrum. Analysis of the spectrum revealed an out-of-plane ring distortion upon ionization, suggesting a transition from the C_S to C_1 configuration. Peaks at unassigned frequencies were attributed to vibrational modes of the D_1 state through time-dependent density functional theory calculations. Natural Bonding Orbital analysis predicted the highest occupied molecular orbital (HOMO) of 2,3-DFP as the π orbital and HOMO-1 as the n_N orbital. Comparison with previous study on 2-fluoropyridine derivative indicates additional impact on the stability of the n_N orbital due to additional fluorine substitution at *m*-position. Our findings shed light on the electronic structure and ionization dynamics of fluoropyridine derivatives, contributing to a deeper understanding of their molecular properties.



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Study on the conformational preference of morpholine using IR resonant VUV-PI mass spectroscopy

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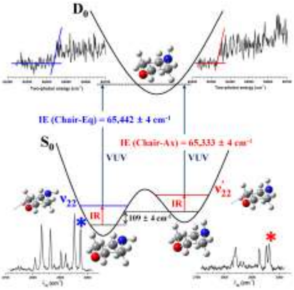
Morpholine [$O(CH_2CH_2)_2NH$], an aliphatic heterocyclic compound, is increasingly utilized in diverse industrial, pharmaceutical, and organic synthesis applications due to its notable nucleophilic properties. This study investigates the intricate conformational properties of morpholine through a combination of advanced mass spectrometric techniques [1, 2] and theoretical calculations. Specifically, infrared (IR) resonant vacuum ultraviolet (VUV) mass-analyzed threshold ionization spectroscopy was employed to measure the unique vibrational spectra of distinct conformers (Chair-Eq and Chair-Ax) in morpholine for the first time. [3] By precisely adjusting VUV photon energy to coincide with vibrational excitation via IR absorption, adiabatic ionization thresholds corresponding to the Chair-Eq (65,442 ± 4 cm^{-1}) and Chair-Ax (65,333 ± 4 cm^{-1}) conformers were determined. This allowed for the accurate assessment of the conformational stability between the two conformers (109 ± 4 cm^{-1}). These findings deepen our understanding on behavior and reactivity of morpholine, offering insights valuable for its applications in organic synthesis and beyond.



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Elucidating the conformational stability of tetrahydrofuran through conformer-specific vibrational spectroscopy

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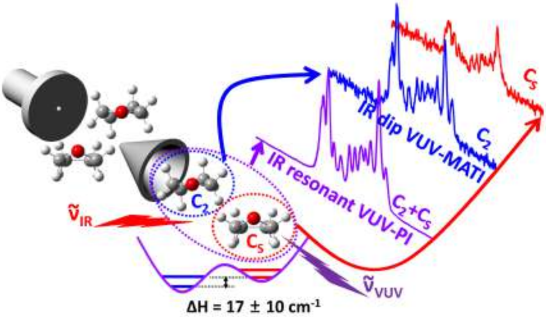
Tetrahydrofuran (THF) plays a pivotal role in numerous biological and chemical processes, its reactivity and interactions heavily influenced by its diverse conformations. Understanding these preferences is essential for grasping its molecular behavior. In this study, we employ IR resonant vacuum ultraviolet photoionization/mass-analyzed threshold ionization (VUV-PI/MATI) mass spectroscopies to analyze the vibrational spectra of individual THF conformers ("twisted" and "bent"). Through conformer-specific vibrational spectra, we determine their relative populations and conformational stability. By selectively ionizing specific conformers, we reveal their coexistence in the neutral state, contrasting with the cationic state where only the twisted conformer persists. These findings offer profound insights into THF behavior with implications across various disciplines.



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Dual frequency comb spectroscopy in the UV region with one million spectral data points resolved

K. Vodopyanov[1] ***, A. Muraviev***[1] ***, D. Konnov***[1] ***, S. Vasilyev***[2]

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We present our frequency comb spectroscopy results performed in the broadband region of the UV portion of the spectrum. The front end of our setup is a dual-comb system consisting of two phase-locked ultrafast Cr:ZnS lasers with the repetition rate 80 MHz and center wavelength 2350 nm. Up to seventh-order harmonic was generated in both channels using multi-grating periodically poled lithium niobate nonlinear crystals, with down to 325 nm UV wavelength (920 THz), corresponding to the short-wave transmission cutoff of lithium niobate. The spectrum of the 6th harmonic frequency comb spans 372-408 nm and contains close to a million comb modes spaced by 80 MHz, while the spectrum of the 7th harmonic (325-343 nm), contains about 500,000 comb lines. These comb lines were resolved using the dual-comb spectroscopy (DCS) technique. In fact, our comb-mode spacing of 80 MHz corresponds, near 390 nm, to the resolving power of 10,000,000 – well beyond the resolution of any modern UV spectrometer. As a demo experiment, we measured, with 80-MHz (comb-line spacing) resolution, the transmission and reflection spectra of a high-finesse volume Bragg grating recorded in bulk photosensitive silicate glass (BragGrate™ Mirror from IPG/OptiGrate) with a narrow (95-pm-wide) UV reflection band centered near 390 nm.

In summary, to the best of our knowledge, this is the first demonstration of the dual-comb spectroscopy in the UV region that provides an ultra-wide coverage and produces high-precision comb-line resolved spectra referenced to a Rb atomic clock. The resolving power of 10 million determined by our comb-line spacing can be further improved by 1-2 orders of magnitude by interleaving the spectra taken with gradually shifted frequency combs, as we demonstrated in our mid-IR experiments.

Comparative investigation of the dissociative photoionization of aniline induced by VUV and UV photons

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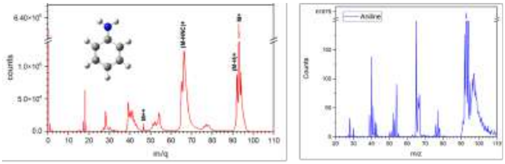
Investigation of dissociative photoionisation of PAHs and PANHs is of great significance in the present astrochemical understanding of our universe. Often such experiments rely on photon energies above the ionization potential to obtain hot monocation of the target molecules. This process introduces ambiguity in the initial state of the dissociation process, since the ion may be produced at various excited configurations. There are alternatives like Thresold-Photoelectron–photoion coincidence (T-PEPICO) or ion storage ring experiments but such measurements are often time consuming and difficult to access. Using aniline as a test case, the present work compares the post-ionisation dissociation process of aninile by two different experiments. Dissociative photoionisation via a single high energy photon is compared with a low energy multistep multiphoton process. The former experiment using VUV radiation is performed using the VMI end station at the GASPHASE beamline of the Elettra - Sincrotrone facility, Trieste [1]. These results are compared with a nanosecond UV pulsed laser at the Atomic and Molecular Physics (AMP) Laboratory at IIST using a High-Resolution energy-selective time of Flight Mass Spectrometer.

Given the approximately 1.3 eV difference between the ground (D0) and first excited (D1) electronics states of the aniline monocation [2], the 290 nm laser pulses will induce dissociation at the ground electronic state (D0) of the aniline monocation by the n-photon process. Strong similarity between multiphoton ionisation driven dissociation and VUV dissociation in terms of mass spectra suggests that the statistical dissociation of aniline cation predominantly occurs in the ground electronic state. [13]



a) Aniline mass spectrum taken at 23eV photon energy b) Aniline mass spectrum taken at 290nm wavelength photons

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[13] One of the authors [MS] acknowledges the receipt of a fellowship from the ICTP Programme for Training and Research in Italian Laboratories, Trieste, Italy.

Analysis of the room temperature absorption spectrum of ethylene in the 6000-8050 cm^{-1} range

O. Ben Fathallah[1] ***, A. Campargue***[1] ***, S. Beguier***[1] ***, L. Manceron***[2] ***, M. Rey***[3]

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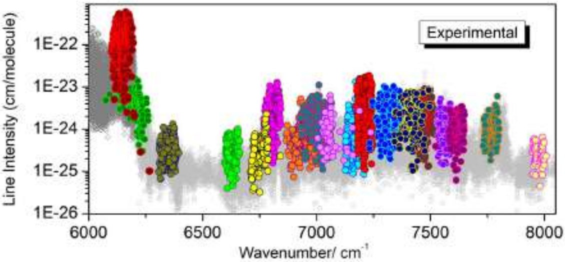
The analysis of the room temperature absorption spectrum of ethylene (C_2H_4) within the spectral range of 6000–8050 cm^{-1} is important for trace detection applications. An experimental list of approximately 46,000 lines was retrieved from a spectrum recorded by Fourier transform spectroscopy at 296 K (P = 15.72 mbar, L = 45 m). Additionally, two spectra at 130 K (P = 0.25 mbar and 3.37 mbar) provided complementary information in two spectral intervals: 6020-6209 cm^{-1} (5900 lines) and 6209-6320 cm^{-1} (3300 lines). From position and intensity matching with a line list derived from variational calculations of $^{12}C_2H_4$ transitions [1], a total of 4,330 transitions were successfully assigned to 18 distinct bands. The assignments were systematically validated using Lower State Combination Difference (LSCD) relations, ensuring consistency for 1839 higher state energies determined through multiple transitions. The analysis of the temperature dependence of the line intensities between 130 and 296 K provides an additional validation of the lower state energy values. Overall the total intensity of the assigned transitions represents 40 and 52% of the total variational and experimental intensities at 296 K in the region, respectively.



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Invited Speaker ThA

Thursday 5 September, 9:00

Chair: O. Dopfer

Room B

Precision Rydberg spectroscopy in H, He, H_2 and He_2

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[1] ETH Zurich (Switzerland)

High-resolution spectroscopic measurements in few-electron atoms and molecules are increasingly used as a means to test the foundations of the theories of atomic and molecular structure. Modern first-principles calculations of the energy-level structure of atomic and molecular systems with up to three electrons consider all interactions in the realm of the standard model of particle physics [1, 2, 3, 4, 5]. Systematic comparisons of the results of such calculations with precise spectroscopic measurements in simple atoms and molecules such as H, He, H_2^+, H_2 and He_2^+ aim at searching for effects not yet included in the theory and at reducing the uncertainties of physical constants.

In this talk, I will present precision spectroscopic measurements of transitions to high Rydberg states of H, He, H_2, and He_2 which we use to determine precise values of their ionization energies and, in the case of H_2 and He_2, also of the spin-rovibrational energy-level structure of H_2^+ and He_2^+. The talk will describe our experimental strategy to overcome limitations in the precision and accuracy of the measurements originating from the Doppler effect, the Stark effect, and the laser-frequency calibration. The experimental results will then be compared with the results of first-principles calculations that include the treatment of finite-nuclear-size effects and relativistic and quantum-electrodynamics corrections up to high order in the fine-structure constant. Recent aspects of these investigations include a new determination of the Rydberg constant as a contribution to the resolution of the proton-size puzzle [6], a new method to record Doppler-free single-photon excitation spectra in the visible and the UV spectral ranges [7], and the “zero-quantum-defect” method to determine the energy-level structure of homonuclear diatomic molecular ions such as H_2^+ [8].

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Cold ion trap IR spectroscopy of ion selective molecular systems

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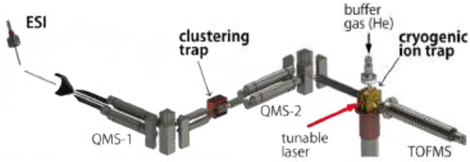
Ion-selective systems play important roles for life. For example, ion channels permeate specific ion through cell membranes, and control the balance of ion concentrations in the cell. On the other hand, antibiotic ionophores capture specific ions, go through the cell membrane, and break the ionic balance to kill the cell. Artificial ion-selective molecules, such as crown ethers, have many applications in our everyday products. Generally, these molecules do not demonstrate their ion-selectivity under isolated conditions. Thus, hydration is indispensable for the ion-selectivity. However, its mechanism in the molecular level has not been established.

In this work, cryogenic ion trap spectroscopy was applied to hydrated ion-selective molecular systems to reveal the hydration effect on the ion-selectivity. A complex of an ion-selective molecule and an ion is generated by electrospry (ESI). Through a first mass-selector (QMS-1), it is introduced to the clustering trap, where it is cooled down moderately and hydrated by introducing water vapor. The hydrated clusters are size-selected by a second mass-selector (QMS-2), and finally stored in a cryogenic ion trap and cooled down to 10 K. Here, tunable lasers are introduced and optical spectra are measured by detecting photo fragments by a time-of-flight mass spectrometer.

We applied this technique to metal ion complexes of selectivity filter of K+ channel [1], several ionophores [2], etc. In my talk, our recent progress of these works will be introduced and roles of the hydration on the ion-selectivity will be discussed.



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Poster Session 2
Thursday, September 5, 11:30

Line lists for four isotopologues of ammonia, NH_2D, $^{15}NH_3$, ND_3, and ND_2H

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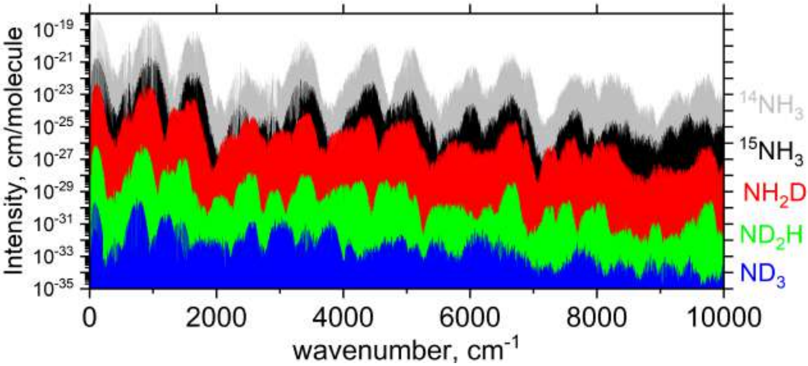
We present theoretical rotation-vibrational line lists for four isotopologues of ammonia, $^{15}NH_3$, NH_2D, ND_2H and ND_3, computed using the variational program TROVE. The spectroscopic model is based on an empirical potential energy and *ab initio* dipole moment surfaces developed and used for the production of the ExoMol line list CoYuTe [1] for $^{14}NH_3$. The line lists range up to 10 000 cm^{-1} and cover the rotational excitations up to $J = 30$. To improve the accuracy of the line positions, the theoretical energies are replaced with experimentally-derived energy levels, where available, produced using the MARVEL procedure. Comparison with the recent experimental spectra show excellent agreement and illustrate the potential of the line lists for atmospheric and spectroscopic analyses. The original MARVELisation of the CoYuTe line list for $^{14}NH_3$ [2] has been also updated as part of this study using line positions from recent experimental publications. The line lists in the ExoMol format will be made available at `www.exomol.com`.



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

V. Stoyanov[1] **, *A. Pashov***[1]

[1] Sofia University "St. Kliment Ohridski", Faculty of Physics, Blvd James Bourchier 5, 1164 Sofia (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 examine the HFS of the $a^3\Sigma^+$ states of the KRb molecule. Accurate potential energy curve for this electronic state was obtained [1] by analysis of fluorescence spectra in heat pipe, after excitation of mixed singlet-triple ($c^3\Sigma^+$, $B^1\Pi$) terms from the ground $X^1\Sigma^+$ state levels. However, no quantitative description has been made so far for the HFS of the $a^3\Sigma^+$ state, even though cold Feshbach [2] and photoassociated [3] molecules were successfully formed and thereafter transferred via Stimulated Raman adiabatic passage to the ground $(v'' = 0, J'' = 0)$ $X^1\Sigma^+$ state.

Optical-optical double resonance saturation spectroscopy in Λ-type configuration is used, where the spin-orbit coupled ($c^3\Sigma^+$, $B^1\Pi$) states served as an intermediate step. We report the current experimental results.

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High resolution infrared spectroscopy and analysis of the spectrum of isotopically chiral *trans-c*-2,3-di-deutero-oxirane and further isotopomers

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Isotopic chirality introduces a completely new isotope effect arising from the parity violating weak nuclear force [1, 2, 3], and is for that reason of fundamental interest, with possible astrophysical applications as well. Oxirane (ethylene oxide *c*-C_2H_4O), detected in Sgr B2N [4], has two isotopically chiral isotopomers, monodeuterooxirane (*c*-C_2H_3DO) and *trans-c*-2,3-dideuterooxirane (*trans-c*-CHD-CHDO). We have previously reported the analysis of high resolution GHz and THz spectra of *c*-C_2H_3DO [5] and *trans-c*-CHD-CHDO [6]. Following this work, Müller et al. have reported a tentative detection of c-C_2H_3DO and the achiral *trans-c*-CD_2CH_2O toward IRAS 16293-2422B [7]. Here we report results of the analysis of the laboratory spectrum of *trans-c*-CHD-CHDO, recorded at Doppler-limited resolution (0.0015 cm^{-1}) up to 3600 cm^{-1} with the Bruker IFS 125 HR Zürich Prototype (ZP 2001) Fourier Transform spectrometer, obtained using the ground state molecular parameters for *trans-c*-CHD-CHDO [6] and Watson's A reduced effective hamiltonian in the I^r representation. The results will be discussed as they pertain to isotopic chirality and molecular parity violation.

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Highly accurate thermochemical properties of the vinoxy radical

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The vinoxy radical is an important intermediate in combustion processes, yet experimental investigations face considerable challenges obtaining accurate estimates of its thermochemical quantities. As a result, computational studies account for the bulk of the Active Thermochemical Tables (ATcT) provenance for vinoxy, with the uncertainty for the ATcT enthalpy of formation lingering near 0.6 kJ/mol. Due to the large geometry change upon ionization of vinoxy, it is difficult to establish the adiabatic ionization energy experimentally. The current adiabatic ionization energy quoted by ATcT via solely computational means is over 19 kJ/mol lower than experimental determinations, accompanied by an uncertainty of 1.5 kJ/mol.

In an attempt to reduce the ATcT uncertainties of these quantities, we apply an extended version of the HEAT model chemistry that is currently under development to the vinoxy radical and its associated cations. These treatments elucidate bond energies of small molecules containing first- and second-row atoms to within 20 cm^{-1}. Composite techniques provide very accurate zero-point energies for use in the thermochemical protocol and fundamental vibrational frequencies that are in excellent agreement with recent experiments. Anharmonic resonances are reanalyzed, suggesting an uncharacteristically complex CH stretching region.

Line strength analysis of the highly excited vibrational states of H_2S: the first decade of $H_2{}^{32}S$

O. N. Ulenikov[1] **,** ***E. S. Bekhtereva***[1] **,** ***O. V. Gromova***[1] **,** ***E. V. Gappel***[1] **,**
C. Sydow[2] **,** ***S. Bauerecker***[2]

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High resolution spectra of the $H_2{}^{32}S$ hydrogen sulfide were recorded with a Bruker IFS 125HR Fourier transform infrared spectrometer and analyzed in the region of 7300–7900 cm^{-1} where the $3\nu_1$, $2\nu_1 + \nu_3$, $\nu_1 + 2\nu_3$, $3\nu_3$, $2\nu_1 + 2\nu_2$, $\nu_1 + 2\nu_2 + \nu_3$ and $2\nu_2 + 2\nu_3$ ro-vibrational bands of the so-called first decade of H_2S are located. Thanks to the improvement of the experimental conditions (in particular, an increase in both the instrumental resolution and the effective absorption path length by 1.5 times), on the one hand, and of the use of a more correct Hamiltonian model (which additionally takes into account the interactions of the bands under study with the $\nu_1 + 4\nu_2$, $4\nu_2 + \nu_3$ and $6\nu_2$ bands), on the other hand, the information obtained as a result of the analysis of the experimental data has been significantly expanded and improved compared to the previous status. The strength analysis comprise more than 900 lines (about 1000 transitions) with maximum values of the quantum numbers J^{max} = 15 and K_a^{max} = 12 and was performed by the fit of the experimental line shapes with a Hartmann–Tran profile. The 15 effective dipole moment parameters were obtained from the weighted fit which reproduce the initial experimental line strengths with the d_{rms} = 2.8%. [14]

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[14] The study was partially supported by the CSU NMNT TPU, Russia (RF MES project #075-15-2021-710).

Towards a theoretical ro-vibrational line list of methanol CH_3OH

O. A. Smola[1] **,** ***S. N. Yurchenko***[1] **,** ***J. Tennyson***[1]

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Methanol and its isotopologues are known for being interstellar weeds, the spectra of which saturates the FIR and IR regions, potentially obscuring other species of astronomical interest [1]. Thus far, a comprehensive ro-vibrational line list for methanol, which might help to disentangle such spectra is missing from the literature. As part of the ExoMol project [2] we aim to bridge this gap, by utilising a newly computed 12-dimensional *ab initio* potential energy surface (PES) and dipole moment surface (DMS) of CH_3OH, obtained at a high level of theory, using the quantum chemistry code MOLPRO [3] and represented using a symmetry adapted coordinate system. The potential energy surface is then used as input for the variational nuclear motion calculation using the symmetry adapted C_{3v}(M) basis set as implemented in the variational Fortran 90 code TROVE [4]. The resulting line list will be improved by fitting our new PES to empirically determined MARVEL [5] levels derived from all available experimental sources, and replacing variational energies with these empirical levels to improve line positions.

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Ro-vibrational analysis of high-resolution FTIR spectra of the ^{13}C-enriched mixture of isotopologues of HCFC-22 ($CHClF_2$) in the 750–850 cm^{-1} spectral region

I. M. Efremov[1]***, E. O. Dobrolyubov***[1]***, S. V. Krasnoshchekov***[1]***, V. B. Laptev***[2]***, S. A. Klimin***[2]***, O. V. Naumenko***[3]

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HCFC-22 ($CHClF_2$) is an important atmospheric pollutant and its high-resolution spectra IR for most abundant isotopologues (^{35}Cl,^{37}Cl) were studied in a number of publications [1, 2, 3]. However, so far the high-resolution spectra for vibrationally excited states of two ^{13}C isotopologues were not investigated. In this study, the ro-vibrational analysis of the high-resolution vibration-rotation spectra of $CHClF_2$, enriched in ^{13}C by 30%, was conducted in the range of 750-850 cm^{-1}. The spectrum was recorded at room temperature, optical path-length of 600 cm and the pressure of 3 torr using Bruker IFS-125HR Fourier transform spectrometer.

The inverse problem of fitting the Watson-type effective Hamiltonian for the polyad including $\nu_4, 2\nu_6$ was solved with accounting of Fermi- and Coriolis-type resonance interactions. The intensities were calculated using the non-empirical dipole moment operator, obtained using the fourth-order Van Vleck operator perturbation theory, and the vibration-rotation wave functions of the fitted effective Hamiltonian. New line lists of isotopic modifications, sets of energies and spectroscopic parameters of effective Hamiltonians were obtained.

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A multi-level excitation diagram analysis method applied to TiO detected at high spectral resolution in the envelope of the variable star χ Cyg

E. Döring[1]***, J. H. Lacy***[2]***, R. S. Giles***[3]***, T. K. Greathouse***[3]***, T. F. Giesen***[4]***, G. W. Fuchs***[4]

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Cosmic dust is formed by nucleation processes in the vicinity of evolved stars. Small molecules of refractory materials formed during these nucleation processes play an important role in dust formation and are also involved in the opacity process of variable late-type stars, as has been shown for the molecule TiO [1]. Recently we presented the high resolution infrared spectrum of TiO and its isotopologues, measured in the laboratory around 10 μm [2]. Using the TEXES instrument on IRTF in its high resolution mode [R =100,000] together with the laboratory data allow unambiguous identification of molecules and enable line shape analysis of the observed molecular spectra. Over a time period of three years various stellar phases of χ Cyg around 970 cm^{-1} were observed with the TEXES instrument. TiO was detected in the mid-IR region, for the first time. Using a home made data analysis software, it was possible to perform an excitation diagram analysis to determine the non-equilibrium temperature and column density of TiO in the envelope of χ Cyg.

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Multi-level excitation diagram analysis of infrared high resolution observations of small astrophysical molecules around late-type stars

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Instead of using the standard spectroscopic tool “rotational diagram” we present an extended version (“multi-level excitation diagram method”) that also works in non-equilibrium ($T_{\mathrm{rot}} \neq T_{\mathrm{vib}}$) environremnts, assuming that the concept of temperature is still valid per vibrational level. With this, high-resolution infrared data taken with the TEXES instrument at the IRTF telescope on Mauna Kea and the EXES instrument on the airborne telescope SOFIA are analyzed. Small molecules, like SiO and its isotopologues and NH_3, are investigated that can be seen in the molecular layers around late- taype stars such as the hyper-giant VY CMa, or variable stars like o Cet, χ Cyg, or IK Tau. Since the spectra show that the rotational and vibrational excitations are not in equilibrium we use the multi-level excitation diagram approach where the rotational and vibrational excitations are treated seper- ately to obtain the individual rotational and overall vibrational temperatures and to finally determine the total column denisities of the species. In princi- ple, the concept can also be extended for electronic transitions, but this is not worked out for this presentation. The results are put in context to the physi- cal environments in which the molecules exist in space and compare existing interpretations and models of these objects with our findings.

Room-temperature $CH_3C^{14}N$–O_2 pressure-broadening line-shape parameters in the 180–1400 GHz range

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Methyl cyanide CH_3CN is a molecule of atmospheric interest, now included in the HITRAN database [1]. However, except for some experimental studies of line intensities, positions, broadening and shifting parameters [3, 3], its line broadening by many atmospheric gases remains incomplete. Besides N_2-broadening, perturbation by molecular oxygen is one of important cases for the terrestrial atmosphere. In the present work, which follows our recent study of the CH_3CN-N_2 system [4], we consider O_2-broadening coefficients of $CH_3C^{14}N$ rotational transitions for a wide range of rotational quantum numbers J and K.

Experiments were performed with a frequency-modulated spectrometer operating in the 50–1500 GHz range [5] and consisting of a 10–20 GHz frequency synthesizer followed by a frequency multiplier chain based on solid-state devices, a 1.1 meter long absorption inox cell and a bolometric detection. Measurements were done at room temperature, with the active-gas pressure equal to 2–5 mTorr and the buffer-gas pressure 50–600 mTorr. Rotational lines with $J = 9, 12, 15, 21, 27, 33, 42, 48, 63, 69, 75$ and $K \leq 15$, located in the region 184–1390 GHz, have been studied in detail. All recorded lines exhibit clear departures from the usual Voigt profile and have been analyzed using the more realistic Speed-Dependent Voigt profile. The Voigt profile has been also employed because of its continuing use in atmospheric applications.

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Temperature dependence of CH_3CN–N_2 line-broadening coefficients

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Reliable modelling of radiative transfer in the terrestrial and planetary atmospheres requires precise knowledge of spectroscopic parameters even for minor compounds such as methyl cyanide (acetonitrile) CH_3CN. This gas is known as one of long-living pollutants produced by biomass burning and industrial processes. One of the key spectroscopic parameters is the collisionally induced line width dependent on the collision partner and the temperature of the medium. For both Earth and Titan atmospheres, the buffer gas of prime importance is molecular nitrogen. To the best of our knowledge, the line-shape parameters of CH_3CN have been studied experimentally solely at room temperature, whereas a larger temperature interval is required.

For the N_2-broadening case, we published some years ago [1] semi-empirical [2] theoretical estimates of line-broadening coefficients and their temperature-dependence exponents in the ν_4 band for the temperature ranges 90–170 K and 250–340 K but the set of experimental values used for fits of our model parameters was limited to $J \leq 48$ [3]. Owing to recent extended measurements in the purely rotational band [4] (J values up to 75), we can now update our calculations of temperature-dependence parameters.

The semi-empirical method is employed, since for many molecular systems its model parameters were shown to be temperature independent. In this way, the 5 model parameters c1-c5 obtained from fits on some room-temperature measurements are used to calculate line-broadening coefficients for various temperatures in an enlarged temperature range; the temperature-dependence characteristics are further deduced using the traditional exponential law and/or the double-power law [5].

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Composite absorption cross sections and integrated band intensities of CHF_3 in air

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CHF_3 (fluoroform, HFC-23) is a by-product in the manufacture of PTFE (e.g., Teflon), refrigerants, fire extinguishing agents and foams. It is a strong potent greenhouse gas with its atmospheric amount fraction increasing by 0.75±0.02 pmol/mol/year [1].

In the current work, we obtained the cumulative spectrum of CHF_3 in mixtures with nitrogen at 296 K in the region of 550—2000 cm^{-1}, following an averaging procedure, developed and used in our recent publications on CF_4 [2] and SF_6 [3]. An assumption of the method that the contribution of self-broadening is negligible might falter for polar molecules already at relatively high dilutions. In case of fluoroform, we see a hint of self-broadening influence for absorber dilution ratios exceeding 1 %. This can potentially lead to a distortion (broadening) of the cumulative absorption cross sections compared to those corresponding to strongly diluted samples. On the positive side, this effect does not affect integrated intensities.

We report the integrated intensities in the region of the ν_3, ν_4 and ν_2/ν_5 fundamental bands together with the overtone band of ν_6, two combination bands $\nu_2 + \nu_6$ and $\nu_2 + \nu_3$, as well as a difference band $\nu_4 - \nu_6$. The expanded uncertainties ($k = 2$) are below 1.8 % for the fundamental bands investigated.

The measurements and analysis were performed within the frame of the EMPIR project “Metrology for Climate Relevant Volatile Organic Compounds” (MetClimVOC) [4]. The spectra were recorded using a Bruker IFS 125HR spectrometer at the PTB FTIR infrastructure.

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In silico assessment of radiative efficiencies and application to halocarbons

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This contribution presents a computational tool based on quantum chemical (QC) methods to evaluate the radiative efficiencies (REs) of greenhouse gases by calculating their infrared (IR) absorption cross-section spectra including a full quantum treatment of anharmonic effects. RE is a crucial metric used in IPCC and WMO reports for climate impact assessments and mitigation strategies. Traditionally, REs are derived from experimentally measured IR absorption spectra, but obtaining high-quality IR spectra can be challenging, especially for species with low vapor pressures. QC approaches are increasingly used to predict spectroscopic properties [1], indeed recent literature and the WMO/UNEP Ozone Assessment report [2] have QC methods for estimating some REs. However, these determinations rely on the double-harmonic approximation that neglecting anharmonic contributions leads to significant deviations from experimental observations. In fact, it has been reported that IR transition strengths for HFCs are overestimated by 5% to 20%[3]. We have developed a cost-effective QC protocol including both mechanical- and electrical-anharmonicity, capable of delivering an accuracy comparable to experimental measurements. We have demonstrated the accuracy of our QC RE tool by considering a set of representative halocarbon compounds, including CFCs, HCFCs, HFCs, hydro-fluoro- and hydro-chloro-fluoro-ethers (HFE and HCFE), and halons. REs were computed with an average accuracy of 5% using double-hybrid functionals, outperforming the widely-used B3LYP functional. Finally, we have applied this methodology to species of atmospheric and industrial relevance with contradictory or limited data, demonstrating the robustness of our approach and its potential to provide reliable data for policy regulations and for screening replacement compounds, thus supporting more effective climate action strategies.

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The nano-lego tool for accurate equilibrium structures from DFT computations

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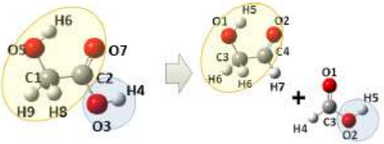
Structure-property relations result from the balance between intra- and intermolecular interactions. In this respect, the knowledge of gas-phase molecular geometries is instrumental for the disentanglement of stereo-electronic, vibrational and environmental effects that define the observed behaviour. The determination of equilibrium geometries for molecules of increasing size is not straightforward from both experimental and theoretical viewpoints. While post-Hartree-Fock methods can be used to obtain reliable equilibrium structures, the size of the treatable systems is hampered by the computational cost. Density functional theory (DFT) offers an effective trade-off between reliability and size-scaling, however the accuracy of DFT structures can be too limited for high-resolution spectroscopic applications. In this contribution, the SE127 database of semi-experimental (SE) equilibrium geometries of molecules containing H, B, C, N, O, F, P, S, Cl, Br and I atoms is compiled. The analysis of the deviations of the structural parameters obtained by PW6B95 and rev-DSDPBEP86 density functionals from the SE values shows that their accuracy can be improved by a linear regression approach (LRA). Finally, the combination of templating fragments taken from the SE127 library together with the LRA for the missing inter-fragment parameters is exploited to develop the nano-LEGO tool for the determination of equilibrium structures [1, 2]. Several case studies demonstrate that it provides geometries on par with composite wave-function methods, but it can treat medium- to large-size molecules. The accuracy in the structural parameters is mirrored on rotational constants that can be predicted with an error around 0.2% [3].



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Impact of water vapor continuum changes on radiative efficiencies

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The outgoing long-wave radiation is crucial for Earth's energy balance. The atmosphere absorbs most thermal radiation emitted from the surface, but it is relatively transparent in certain windows. While water vapor dominates the infrared atmospheric spectrum, the windows existing between its vibrational bands are characterized by the water vapor continuum [1]. As a result, the sum of line-by-line H_2O transitions does not reproduce the observed absorption profile. To assess this effect, the MT_CKD (Mlawer-Tobin_Clough-Kneizys-Davies) model is used as an empirical parametrization of the H_2O continuum. The model is regularly updated with new observational data [1] and the recently MT_CKD versions 4.2 and 4.3 introduced significant changes. Version 4.2 adjusted self- and foreign-continuum coefficients in the 590 - 1400 cm^{-1} window and version 4.3 added new foreign-continuum coefficients above 4000 cm^{-1}. These changes address the issue of strong self-continuum leading to less downwelling longwave flux and an increased outgoing long-wave radiation. Previous studies analyzed the impact of MT_CKD versions on the atmospheric radiative forcing (RF) finding only modest variations [2]. The present contribution assesses how updates in MT_CKD affect the RF curve proposed by Pinnock et al. [3] and estimates their impact on the radiative efficiency (RE), i.e. the RF unit gas concentration, for different halocarbons. REs are estimated by using IR absorption cross-section spectra quantum-mechanically simulated beyond the double-harmonic approximation. Changes in RE due to the inclusion of the 0-500 cm^{-1} spectral region, often challenging for experimental measurements of REs [4], are also addressed.

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Vibrational-rotational properties and climate metrics of HCFC-132b

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Among climate change drivers, halogenated organics significantly contribute to global warming and, if chlorinated or brominated they catalyze ozone depletion (OD). A gas'greenhouse capacity is measured by the radiative efficiecy (RE) and global warming potential (GWP) climate metrics, which depend on its infrared (IR) absorption cross section and its atmospheric lifetime. Hydro-chloro-fluoro-carbons (HCFCs), introduced as replacements of chloro-fluoro-carbons, have been banned by the Montreal and Kyoto protocols, due to their O potentials and important GWPs. Despite these regulations, atmospheric concentrations of some HCFCs have increased, and recently HCFC-132b has been detected [1]. This molecule has no known end-uses, hence it escaped any spectroscopic investigation, while the RE and GWP have been determined from IR spectra simulated within the harmonic approximation [2]. In this study, the rotational-vibrational spectroscopic characterization of HCFC-132b was performed by coupling IR spectroscopy and quantum chemical calculations. Rotational spectroscopic parameters were computed by CCSD(T)-based composite schemes and the IR absorption cross section spectrum, simulated beyond the double-harmonic approximation, was used to assign the IR spectrum experimentally acquired in the 150 - 3500 cm^{-1} range. The interplay between theory and experiment reveals that the observed spectrum features the presence of two different rotamers. Finally, from the IR absorption cross section measured experimentally, the RE and GWP were determined, showing that the values in the WMO 2022 report [2] are overestimated by about 10

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Laboratory rotational spectroscopy of potential interstellar molecules

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The detection of so-called complex organic molecules (COMs) in the interstellar medium (ISM) directly probes the physical and chemical environments in space. In particular the chemical evolution of dense regions of the interstellar medium, especially around newly formed stars, and ultimately, the formation of planets. To date, over 300 molecular species have been identified in the ISM and circumstellar regions facilitated by radio astronomical observation enabled by accurate laboratory rotational transition frequencies. We have investigated the rotational spectra of potential interstellar COMs and carried out astronomical searches for these molecules in the ISM. In this contribution, we will present the recent rotational spectroscopic investigations of some CN and NCS bearing COMs. These precise laboratory rotational spectroscopic data set is fundamentally important for observational astrochemistry.

Accessing all vibrationally excited states of the $X^+\ ^2\Sigma_u^+$ ground electronic state of He_2^+ through multi-step laser excitation

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Precise spectroscopic measurements in small molecular systems such as He_2 and He_2^+ is of significant interest as benchmark to *ab-initio* quantum-chemical calculations [1, 2, 3]. In the case of He_2^+, only the lowest ($v^+ = 0 - 2$) [4, 5] and very highest ($v^+ = 21 - 23$) [6] vibrational levels of the $X^+\ ^2\Sigma_u^+$ electronic ground state have been characterised experimentally. In this poster, we describe a method to access all vibrational states of He_2^+ $X^+\ ^2\Sigma_u^+$ from $v^+ = 0$ to $v^+ = 23$ using a multi-step excitation scheme. The approach involves the production of a supersonic beam of He_2 in the long-lived metastable a $^3\Sigma_u^+(v = 0 - 2)$ states through an electric discharge. A pulsed laser promotes the system to a selected excited vibrational level of the c $^3\Sigma_g^+$ electronic state with v' in the range $3 - 5$. These states predominantly decay radiatively to the a $^3\Sigma_u^+$ state with $v \geq v'$ because of favorable Frank-Condon factors. A second laser is then employed to induce transitions from these vibrationally excited a $^3\Sigma_u^+(v)$ metastable states to vibrationally excited He_2^+ $X^+\ ^2\Sigma_u^+(v^+ \geq v)$ states. High-resolution photoelectron spectra of these ionizing transitions are recorded using the technique of pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. In another experiment, the second laser is used to directly photoionise the intermediate state c $^3\Sigma_g^+(v', N')$ to the state $X^+\ ^2\Sigma_u^+(v^+, N^+)$ levels and record PFI-ZEKE photoelectron spectra. With these excitation schemes, spectra of $X^+\ ^2\Sigma_u^+(v^+, N^+)$ rovibrational levels of He_2^+ could be measured for the first time from the ground ($v^+ = 0, N^+ = 1$) rovibrational level all the way up to the dissociation limit. These new results will be compared with the predictions of *ab-initio* quantum-chemical calculations.

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Rotational spectroscopy of secondary organic aerosol precursors: prenol and trans-2-hexenal

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Biogenic volatile organic compounds (BVOCs) are crucial to the chemistry of the troposphere, significantly influencing air quality and climate change on both local and global scales. Among these, isoprenoids and Green Leaf Volatiles (GLVs) such as 3-methyl-2-buten-1-ol (Prenol) and trans-2-hexenal (T2H) stand out due to their unsaturated carbon-carbon (C=C) double bonds [1], which greatly enhance their reactivity with atmospheric oxidants. These compounds are emitted by vegetation under stress and serve important roles in various industrial and environmental processes; T2H is utilized in perfumery and has been identified as an aerosol precursor [2], while Prenol is used as a biofuel [3], with ongoing research into its role in aerosol formation. We present here the rotational spectroscopy of prenol and T2H studied using a free jet Fourier-transform microwave (FTMW) spectrometer (8 to 18 GHz), supported by quantum chemistry calculations. These molecules feature rotating single bonds, allowing for multiple conformer formations. Our observations on Prenol allowed us to identify its lowest energy conformer and simulate its Watsonian rotational parameters. Room temperature millimeter-wave measurements have been also performed allowing to refine the ground state constants, to measure rotational lines in the lowest energy vibrational levels and to produce a linelist for monitoring applications. Meanwhile, our observations of T2H led to the identification of at least three conformers, highlighting its complex structural dynamics. This work aims to studying the hygroscopic properties of associated aerosols by examining the microsolvation of these molecules and their oxidation products.

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Conformational mapping, interactions, and fluorine impact by combined spectroscopic approaches and quantum chemical calculations

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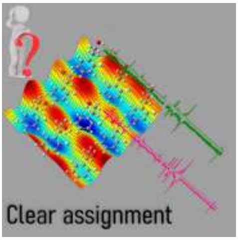
Noncovalent interactions and their careful variation can be crucial in understanding molecular structures, conformational topographies, and properties. Here, we examine the fluorination impact on the structure and conformational behavior of 2-(2-fluorophenyl)ethyl alcohol (2-FPEAL) by monitoring the first individual ionization-loss-stimulated Raman spectra of the jet-cooled molecule [1]. The comparison of two different broad-range spectra and predicted equivalents discloses two distinct structures. One possesses a folded side chain (*gauche*) and the other an extended chain (*anti*) with the terminal hydrogen atom pointing opposite or toward the fluorine side, indicating the improper previous tentative assignment of the latter. These conformers resemble and differ from the nonfluorinated analog structures. Theoretical analyses reveal interconversion pathways of 2-FPEAL conformers during expansion and the delicate balance between attractive (C-H$\cdots$F and O-H$\cdots\pi$) and repulsive interactions. These findings suggest that the relative energies of conformers are not always the key factors determining their appearance and exhibit the achievements of our unique integrated approach and specifically its potential for overcoming future structural challenges.



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Formation of radicals and small molecules in laser-induced plasmas

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Laser-induced breakdown spectroscopy (LIBS) is widely used to determine the elemental composition of samples. Usually, the emission of single atoms and ions is determined in order to examine the composition of a sample. However, there are several elements exhibiting very weak emission lines in LIBS measurements (e.g. halogens). During the cool-down process of the laser induced plasma usually the evaporated atoms form several radicals and molecules (some of these exist just a short time before reacting further). In some cases the radicals or molecules of these elements have stronger emission lines then the elements forming the radicals or molecules. This may lead to lower detection limits. In order to study the formation process of radicals and molecules we performed both experimental examinations and simulation calculations. We studied the generation of several diatomic radicals consisting of cations Ca^{2+} and Al^{3+}, and anions like F^-, Cl^-, and O^{2-}. The used laser pulses had a pulse duration in the range from µs to fs, and a pulse energy in the range of several µJ to several 100 mJ.

As an application, we measured the diffusion of chloride (e.g. from de-icing salt) in concrete. Quantitative measurement of chloride is of high industrial interest because it allows the estimation of the critical pitting corrosion process and thus the expected lifetime of a concrete structure. In the laser-induced plasma plume chlorine and calcium from the cement react to CaCl radicals with strong molecular emission bands in the visible spectral range, from which the concentration of chloride can be deduced.

A new approach to enhance the sensitivity of THz-TDS

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THz Time Domain Spectroscopy (THz-TDS) is a powerful technique that has been around for three decades. The commercialized broadband technique (0.2-6 THz) offers a dynamic range of $\approx$100 dB making it a go-to technique for characterizing a wide range of materials and systems including gases and molecules of atmospheric interest. The TDS is highly selective [1] and is capable of multi-species detection and identification in complex mixtures. We propose a novel approach that promises to increase the sensitivity of the THz-TDS system when targeting halogenated atmospheric pollutants. The idea is to align a molecular spectroscopic comb of symmetric alky halides (e.g. CH_3Cl, CH_3Br, CH_3I, etc.) and the optical modes of a Fabry-Perot cavity to achieve a strong coupling regime where the molecular lines are split in frequency. Target molecules can be extended to symmetric and linear molecules whose spectra can be considered as frequency combs. We will be presenting the first phases of the development of the new apparatus. We hope this effort will open a new area of applications for the THz-TDS, such as reaction kinetics, and be a step further towards making the THz-TDS a standard analytical technique for gas phase studies.

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Non-LTE infrared spectroscopy of jet-cooled naphthalene and its dissociation products for astrochemical insights

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Polycyclic Aromatic Hydrocarbons (PAHs) are omnipresent in various astronomical objects [1]. Two PAH derivatives: 1- and 2-cyanonaphthalene have been identified very recently in the cold region of the Taurus molecular cloud with the aid of radio astronomy coupled with microwave spectroscopy [2]. However, microwave detection of molecules without a permanent dipole is not possible, as is the case with naphthalene. In this context, IR spectroscopy plays an essential role.

In this work, the IR spectrum of naphthalene was recorded at 12.7 μm using the jet-AILES setup [3] equipping the AILES beamline of the synchrotron SOLEIL, and between 1.65 and 1.7 μm using slit-jet cavity ringdown spectroscopy (CRDS). In the supersonic expansion, an efficient rotational relaxation of naphthalene occurs resulting in a rotational temperature of about 25 K, while the vibrational cooling is limited due to an insufficient number of two-body collisions. This causes an interesting non-LTE situation, favorable for the detection of hot bands. The observed hot bands at 12.7 μm were assigned with the aid of the AnharmoniCaOs software developed by some of us [4]. Non-thermal populations of individual vibrational states from which transitions originate were derived further, allowing us to simulate the non-LTE CRD spectrum recorded in the near-infrared.

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Rationalizing molecular vibration through matrix isolation infrared spectroscopy and vibrational configuration interaction computations

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Matrix-isolation infrared (MI-IR) spectroscopy gives rise to "clean" vibrational spectra. As molecular rotation is quenched, MI-IR provides complementary information to gas-phase IR. However, *matrix effects* are unsystematic and must be evaluated for each system. Vibrational spectra can be computed by solving the time-independent Schrödinger equation, e.g., in a vibrational self-consistent field and configuration interaction (VSCF/VCI) approach for the Watson operator. Using a potential energy surface that includes *anharmonicity* and *mode-coupling*, VCI can achieve spectroscopic accuracy for MI-IR experiments. However, a balance between accuracy and cost must be evaluated for each system. Our systematic combination of VCI and MI-IR confronts theoretical (e.g., electronic structure theory, expansion of VCI space) and experimental (e.g., matrix-analyte ratio, matrix material) aspects. We provide improved vibrational assignments for water [1], methane [2], carbon dioxide [2], fluoroethane [3], carbonic acid[4], methanol [5] discussing matrix shifts and splittings, oligomers, isotopic shifts, resonances, vibrational combination bands and overtones, and rotational-vibrational structure.

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Spectroscopic constants from rovibrational configuration interaction calculations

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Molecular (ro)vibrational spectra from microwave, millimeter wave and infrared experiments are usually represented by rotational and centrifugal distortion constants. These spectroscopic constants are derived from (and usually computed by) perturbation theory. In experiment, transition line lists are taken as reference for fitting an effective Hamiltonian, turning the constants into fit parameters. These constants (or parameters) concisely grasp the essence of a spectrum and, thus, are indispensable when it comes to communication of spectroscopic results.

While "experimental" spectroscopic constants are derived by fitting, their *ab initio* calculation is often based on vibrational perturbation theory (VPT). However, it is well-established that variational approaches, e.g., rovibrational configuration interaction (RVCI), are superior in calculating rovibrational states. Thus, spectroscopic constants from RVCI are desirable.

We here present a procedure, using RVCI [1] calculated rovibrational states and transitions as a reference for fitting Watson's A- or S-reduced Hamiltonian including up to sextic centrifugal distortion [2, 3]. Based on an educated parameter guess from VPT, our procedure becomes very efficient. First tests on small asymmetric top molecules (water, hydrogen sulfide, formaldehyde and thioformaldehyde) show very good agreement with experimentally derived spectroscopic constants [4].

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Spin-rovibrational structure of the molecular hydrogen ion from spectroscopy of Rydberg states

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Precision measurements of rovibrational energies in H_2^+ provide access to fundamental constants such as the proton-to-electron mass ratio or the proton charge radius, by comparison with theoretical results [1]. Because H_2^+ and D_2^+ are nonpolar, pure rotational and vibrational transitions are forbidden in the electric-dipole approximation and are very difficult to measure. As alternative method to determine the energy-level structure, spectra of Rydberg series of H_2 and D_2 converging on different spin-rovibrational states of H_2^+ and D_2^+ can be measured, from which their relative energies are obtained by Rydberg-series extrapolation [2, 3].

As application of this method, we determined the fundamental vibrational interval of H_2^+ by continuous-wave laser spectroscopy of Stark manifolds of Rydberg states of H_2 with the ion core in the ground and first vibrationally excited states [4]. From measurements of Stark manifolds at varying electric field strengths and comparison with precise calculations of the field-induced Stark shifts [5], the zero-quantum-defect positions $-R_{H_2}/n^2$ are determined, which yield precise ionization thresholds. We demonstrate the use of this procedure for the determination of the fundamental vibrational interval of H_2^+ at sub-MHz uncertainty.

This contribution also focuses on the determination of the first three rotational intervals of para-H_2^+ ($N^+ = 2, 4, 6$) and their spin-rotation splittings at sub-MHz accuracy by a combination of precision spectroscopy and multichannel-quantum-defect theory.

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The new ExoMol photodissociation database

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Photodissociation, the process of breaking chemical bonds through photon absorption, plays a crucial role in astrophysics, particularly in understanding the properties of stars and other celestial bodies. However, obtaining accurate photodissociation rates requires integrating flux and cross-section data, posing challenges due to gaps in the photodissociation cross-section database and the strong temperature-dependence of photodissociation rates [1].

To address this issue, the ExoMol project [2], is undertaking a significant expansion of the database to consider processes at ultra violet wavelengths including continuum absorption, predissociation and photodissociation [3]. This project aims to compile temperature-dependent photodissociation cross-section data for over 30 small molecules relevant to astrophysics, filling gaps identified in previous literature [4]. By providing a unified format for photodissociation cross-section data, this initiative simplifies the process for physicists to calculate photodissociation rates and model photon-rich environments, such as the top of exoplanetary atmospheres, more accurately. We are working on extensions to allow the treatment of photodissociation in non-local thermodynamic equilibrium environments, which is important for OH, as well as adding new molecules to the database such as the triatomics HCN and H_2S .

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High-resolution spectroscopic study of vinyl cyanide isotopologues for radio astronomy: $^{13}CH_2CHCN$ and $CH_2CH^{13}CN$

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Vinyl cyanide (C_2H_3CN, VCN), is a molecule of high spectral complexity and one of the most abundant complex organic molecules found in interstellar clouds. It accounts for many pure rotational lines observed there, both from its ground and vibrationally excited states. Astronomical radio emission of VCN in the ground vibrational state may be so strong that the ^{13}C isotopic species can be observed with ease (e.g., Belloche et al. 2016) and, as a consequence, in warm/hot regions of the interstellar medium, vibrational satellites of these species will very likely also contribute substantially to molecular line emission. While the pure rotational and infrared spectra of parent VCN have been studied quite extensively previously, little is known about vibrationally excited states of the ^{13}C isotopic species. Here, we present recent high-resolution infrared spectra of $^{13}CH_2CHCN$ and $CH_2CH^{13}CN$ recorded up to 700 cm^{-1} at the AILES beamline of the SOLEIL synchroton and give a status report on the analysis performed with the Automated Spectral Assignment Procedure, ASAP [2]. Complementary 3 mm chirped-pulse pure rotational spectra obtained at Saclay will also be shown.

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Ab initio structure and vibration-rotation dynamics of aluminum monohydroxide

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The potential energy surface and vibration-rotation energy levels of aluminum monohydroxide in its $\widetilde{X}\,{}^1A'$ electronic state have been determined from accurate ab initio calculations. The inner-core electron correlation, higher-order electron correlation, scalar relativistic, and adiabatic effects were accounted for. The equilibrium configuration of the AlOH molecule was found to be bent, although with the wide AlOH angle of 163° and the small barrier to linearity of just 4 cm^{-1}. The bending minimum-energy potential function $V_{\mathrm{mep}}(\theta)$ was determined to be

$$V_{\mathrm{mep}}(\theta) = -71\,\theta^2 + 441\,\theta^4 + 52\,\theta^6 - 19\,\theta^8 + 5\,\theta^{10}$$

where the potential energy V and the AlOH bending coordinate θ are given in wavenumbers and radians, respectively. The ground bending state of the main isotopologue AlOH was calculated to lie 138 cm^{-1} in energy above the top of the barrier to linearity. The classical turning point for this state is located at the AlOH valence angle of 135°. The AlOH molecule was definitely confirmed to be quasilinear. The predicted adiabatic potential energy surfaces for the AlOH, AlOD, ^{26}AlOH, and Al^{18}OH isotopologues were used to determine the corresponding vibration-rotation energy levels. The spectroscopic constants obtained for these species can be useful in a future analysis of high-resolution vibration-rotation spectra.

Infrared spectroscopic study on nuclear spin conversion of matrix-isolated hydrogen

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The molecular species including hydrogen nuclei in the rotationally symmetric positions has nuclear spin isomers. The interconversion between the isomers is strictly forbidden in the isolated state [1], but is significantly promoted in condensed systems. Because the molecular wave function is required to be antisymmetric with respect to the permutation of protons, there are specific combinations of the rotational and nuclear-spin states. Because of these combinations, infrared absorption spectroscopy combined with the matrix isolation technique has been extensively employed to observe the nuclear spin conversion of polyatomic molecules, such as H_2O [2, 3], NH_3 [4], CH_4 [5, 6]. However, this method cannot be straightforwardly applied to the conversion study of H_2 because its stretching vibration is infrared-inactive. Thus, the author and co-workers trapped and polarized H_2 in a CO_2 matrix with porous structure; from the time evolution of the infrared spectrum, the conversion rate of H_2 was determined to be 9.4×10^{-4} s^{-1} at 5.4 K [7]. In the present study, this work has been extended; the dependence of the conversion rate on the temperatures during the sample deposition and spectral measurement was systematically investigated. In the presentation, the abrupt rises of the matrix temperature during the deposition, which are closely related to the matrix structure, will be also discussed.

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Investigating the rotational spectrum of ^{17}O isotopic formamide: implications for astrochemistry

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Since its first detection in the interstellar medium (ISM) in 1971 [1], formamide (NH_2CHO), known for its abundance in hot cores, has been critical to astrochemistry and prebiotic chemistry. Numerous rotational spectroscopic studies have been conducted since 1955 [1], covering the normal species and isotopologues (^{13}C, ^{15}N, and ^{18}O, see Kryvda *et al.* [3]). The Lille's group has provided data up to 1 THz for the normal species, its ν_{12} vibrational state and the ^{13}C isotopologue [3], enabling the first detection of ν_{12} transitions in ISM. Using the ReMoCA (Re-exploring Molecular Complexity with ALMA) survey, Belloche *et al.* reported the first interstellar detections of $NH_2CH^{18}O$ and $^{15}NH_2CHO$ in Sgr B2(N), with column density ratios of 1/140 and 1/314, respectively, compared to the main isotopologue [5].

The lines of $NH_2CH^{18}O$ identified in the ReMoCA survey have high signal-to-noise ratios, suggesting that lines of the ^{17}O isotopologue of formamide should also be detectable. This motivates further laboratory measurements. We present the millimeter-wave absorption spectrum of the ^{17}O isotopic formamide ($NH_2CH^{17}O$) in the 150-500 GHz range. These data will help identify interstellar spectral lines and improve our understanding of isotopic fractionation and the formation of formamide in space.

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Sub-millimeterwave spectrum of $CH_2{}^{35}Cl_2$, $CH_2{}^{35}Cl^{37}Cl$, and $CH_2{}^{37}Cl_2$ in the $(v_4 = 1)$ vibrational state up to 1.1 THz

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High resolution spectra of methylene chloride in natural abundance are recorded in wide spectral regions from 0.075 up to 1.090 THz (for experimental details, see Ref. [1]). More than 7000 multiplet center frequencies with the value of quantum number $J^{max} = 100$ and $K_a^{max} = 19$ were assigned to the rotational transitions in the $(v_4 = 1)$ excited vibrational state of the three mentioned isotopologues of the methylene chloride molecule. A weighed fit of experimental data allowed us to obtain a set of rotational and centrifugal distortion parameters which reproduce the initial experimental data with the d_{rms} = 20 kHz in the whole region up to 1.1 THz. [15]

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[15] The study was partially supported by the CSU NMNT TPU, Russia (RF MES project #075-15-2021-710).

Rotational fingerprints of 3-amino-1-propene inthe millimeter wave spectral region

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Complex organic molecules [1] represent an important subset of interstellar species. Among them, amines, the species bearing $-NH_2$ functional group, have a significant prebiotic character as they represent plausible key players in the formation of amino acids. In this work, a detailed rotational study of 3-amino-1-propene ($CH_2CHCH_2NH_2$), a larger variant of interstellar vinylamine [2], is presented. The room-temperature rotational spectrum was measured between 204 and 330 GHz using the Prague semiconductor millimeter wave spectrometer [3]. Extended sets of spectroscopic parameters with accuracies conducive to reliable interstellar searches are provided for the four conformational isomers.

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Utilisation of a high repetition discharge nozzle in a molecular beam setup

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Diffuse interstellar bands, DIBs, are spectroscopic features observed in low-density regions of the interstellar medium and are usually associated with the presence of dust. However, the origin of the DIBs is still a big mystery even after a hundred years since their discovery. Probable carriers of those bands are various, yet unassigned molecules found in the visible and near-infrared spectra of bright sources that are thought to be located behind gas and dust clouds. Complex organic molecules may contribute to the DIBs, as shown in recent work by Campbell et al., who assigned some of the near-infrared DIBs to the molecular ion C_{60}^{+} [1]. To assign more DIBs, laboratory experiments are required. One of the challenges is to produce candidate molecules in sufficient amounts for spectroscopic analysis. Therefore, it is necessary to employ a powerful source capable of producing these molecules and couple this source with a high resolution and highly sensitive spectrometer.

In our case we use an Even-Lavie high pressure pulsed valve [2] together with a mountable DC discharge to produce a supersonic jet. In our experiment the molecular species in the jet are adiabatically cooled to about 6 K. In combination with a resonance-enhanced multiphoton ionisation time-of-flight (REMPI-ToF) mass spectrometer and a quadrupole mass spectrometer (QMS), minute quantities of both stable and transient molecules can be detected with our setup. The REMPI-ToF method provides spectra in the optical range that can be directly compared with the DIB spectra, while the mass distribution of the generated molecules and fragments can be detected on the QMS.

Here we present first results from our DC discharge source in a molecular beam setup, coupled with REMPI spectroscopy and a QMS as detection techniques.

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Rotational-vibrational analysis of selected strong fundamentals in $PF^{35}Cl_2$ and $PF^{35}Cl^{37}Cl$

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We report results of the analysis of the high resolution spectrum of $PFCl_2$ with its isotopically chiral isotopomer $PF^{35}Cl^{37}Cl$. The concept of isotopic chirality is of fundamental interest because it introduces a completely new isotope effect arising from the parity violating weak nuclear force[1, 2, 3, 4, 5]. Because of the different electroweak charge of isotopic nuclei with different numbers of neutrons, one can predict a parity violating energy difference $\Delta_{PV}E$ between the ground state energies of the enantiomers of chiral molecules, including isotopically chiral molecules[1, 2]. For $PF^{35}Cl^{37}Cl$ we have calculated $\Delta_{PV}E$ to be about 3.5aeV by our electroweak quantum chemistry approaches [4, 5]. While very small, this can be measured, in principle, by special experiments[1, 2], although no successful experiment has been reported so far [1, 2]. We present here the initial results of the experimental study of $PFCl_2$, related to our previous theoretical study [4]. The infrared spectrum of $PFCl_2$ has been measured with our diode laser spectrometer in a supersonic jet (15–20 K) between 830–834 cm^{-1} and 838–841 cm^{-1}, and with the Bruker IFS 125 HR Zürich Prototype (ZP 2001) Fourier Transform spectrometer (room temperature, 650–1000 cm^{-1}, resolution: 0.0015 cm^{-1}). We analysed the ν_1 fundamental (PF-stretching mode) of $PF^{35}Cl_2$ (ν_0= 836.6148 cm^{-1}). The diode laser spectra at 15 K simplified the spectra considerably, making it possible to detect ν_1 absorption lines of $PF^{35}Cl_2$ and $PF^{35}Cl^{37}Cl$. The results will be discussed as they pertain to isotopic chirality and molecular parity violation.

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Microwave spectrum of the three lowest torsional states of dimethylether $(CH_3)_2O$

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Microwave transitions belonging to the ground and two methyl torsional modes of dimethylether (DME), $(CH_3)_2O$, have been analyzed using a modified version of the PAM_C2v_2tops program suitable for molecules with two equivalent methyl rotors and C2v symmetry at equilibrium [1]. The dataset combines the literature data and previous measurement campaigns (ground state [2], torsional excited states [3, 4]), as well as the new measurements, which have been carried out using the Kharkiv spectrometer in the Institute of Radio Astronomy of NASU (Ukraine) from 49 GHz to 180 GHz and from 255 GHz to 400 GHz. Significant progress in fitting transitions within the first excited torsional states in the two methyl torsional modes in DME has been achieved, and the joint dataset has been reproduced within experimental accuracy by our fit. In the course of our fitting attempts, we have encountered some problems with convergence of the size of the torsional basis set in the two stage diagonalization procedure implemented in the initial version of the PAM_C2v_2tops program [1]. The modification of the PAM_C2v_2tops program which solves this problem as well as details of the experimental dataset, its analysis and the fit will be discussed. [16]

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[16] This work was done under support of the Volkswagen foundation. The assistance of Science and Technology Center in Ukraine is acknowledged (STCU partner projects P686a, P756).

Extensive study of dense rotational spectra of the chiral molecule chlorofluoroacetonitrile

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The high-resolution rotational spectra of two isotopic species of chlorofluoroacetonitrile, namely ^{35}ClFCHCN and ^{37}ClFCHCN, were recorded employing the cavity-based FTMW spectrometer (8–18 GHz) and K- and W-band FTMW spectrometers at the DESY facility in Hamburg, and the THz spectrometer (165–620 GHz) in Kassel. The hyperfine structure of rotational transitions arising from the nuclear quadrupole coupling of the ^{14}N and ^{35}Cl/^{37}Cl nuclei was investigated in the ground vibrational state of both the parent molecule and its ^{37}Cl-substituted species. Additionally, the r_s structural parameters of the molecule were derived via the Kraitchman's equations [1]. Moreover, several vibrational satellites corresponding to the low-lying vibrationally excited states of both isotopic forms were observed in the spectra and analysed. Supported by DFT calculations, the spectral analysis resulted in an extensive dataset counting up to 20,000 transitions and was perfomed with the recently developed General Fitting Code (GFC), a program for a simulation and fitting of rotational and vibrational spectra. The obtained precise sets of molecular parameters provide a basis for a chiral detection of the title molecule by three-wave mixing spectroscopy [2, 3].

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First results of IR–UV double resonance with the cold molecular beam apparatus

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Reconciling high spectral resolution and high sensitivity simultaneously is a daunting task. We have previously shown that we can transfer the precision of the MW radiation into vibrationally excited states employing the double resonance technique using a combination of microwave (MW) and infrared (IR) radiation and therefore improve the spectral resolution by up to three orders of magnitude [1].

Here we present the first results of IR-UV double resonance experiments on acetylene (C_2H_2) conducted with a new molecular beam apparatus. The apparatus allows high-resolution infrared, optical and UV spectroscopy of cold neutral molecules, via resonant multiphoton ionization time-of-flight (REMPI-ToF) mass spectroscopy. A pulsed nozzle is utilized to produce cold molecules in an adiabatically expanding supersonic jet. Two skimmers reduce expanding gas to a molecular beam. We use a high-power (up to 1.5 W) continuous-wave optical parametric oscillator (cwOPO) from *Qioptiq* for an excitation with a subsequent REMPI-ToF detection. The narrow linewidth of the cwOPO (10 - 20 kHz) in the mid-infrared (2.7 - 4 μm) and it's frequency-stability (± 3 MHz) allows to uniquely address ro-vibrational states. The REMPI method provides excellent detection sensitivity even for extremely small samples and mass selectivity.

In the future we plan to use multiphoton excitation via IR light and MW radiation in the form of three-wave mixing (3WM) schemes [2] or by photo-electron circular dichroism (PECD) [3]. When working with chiral molecular species in a cold molecular beam this will allow us to distinguish the enantiomers from each other.

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Fluorescence and mass-selective spectroscopy of small silicon carbides: the $\tilde{C}\,\Sigma_u^- \leftarrow \tilde{A}\,\Sigma_g^-$ transition of *l*-SiCCSi

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In pursuit of reactive silicon-bearing molecules of astrophysical interest, we are carrying out an optical survey of a jet-cooled discharge of silane and acetylene using resonant two-colour two-photon ionization (R2C2PI) and two-dimensional (excitation/emission) laser-induced fluorescence with intensified array detection. For the conspicuous SiC_2 and Si_2C molecules, resolved single-vibronic-level emission (SVLE) spectra spanning several thousand cm^{-1} of the ground-state vibrational energy with high signal-to-noise ratio can now be acquired in a fraction of a second. It is thus feasible to collect an emission spectrum for every step of the laser wavelength and construct a two-dimensional map that quickly exposes characteristic patterns of distinct spectral carriers not obvious in excitation or emission alone. We have in the course of this work measured the strong ($f \sim 0.25$) $\tilde{C}\,\Sigma_u^- \leftarrow \tilde{A}\,\Sigma_g^-$ spectrum of linear SiCCSi by fluorescence, building on previous observations of the origin near 516.58 nm [1, 2]. A matching mass-resolved spectrum is obtained by R2C2PI and excited-state vibrational character probed by SVLE, allowing a complete assignment in terms of the symmetric Si-C stretch and the two doubly degenerate bending modes. A Franck-Condon analysis of the Si-C stretch progression yields a change in bond length commensurate with that obtained from a rotationally resolved band envelope [2]. With the $\tilde{A}$ state serving as intermediate, an adiabatic ionization energy of 7.48 eV is determined. A second band system arising from an isomer with a higher ionization energy is observed with onset near 450 nm, although at the time of writing we cannot speculate as to whether the carrier is the rhomboidal or trapezoidal form [3].

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High-resolution spectroscopy and multichannel quantum-defect-theory analysis of high Rydberg states of rare-gas atoms

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High-resolution spectra of high *n*p and *n*f Rydberg series of Kr and Xe were measured by single-photon excitation from the Rg $(n\mathrm{p})^5((n{+}1)\mathrm{s})^1$ $^3\mathrm{P}_2$ metastable state to study bound Rydberg states located below the $\mathrm{Rg}^+(n\mathrm{p})^5$ $^2\mathrm{P}_{3/2}$ ionization threshold, and autoionizing Rydberg states located between the $\mathrm{Rg}^+(n\mathrm{p})^5$ $^2\mathrm{P}_{3/2}$ and $\mathrm{Rg}^+(n\mathrm{p})^5$ $^2\mathrm{P}_{1/2}$ ionization thresholds with $\mathrm{n} = 4$ and 5 for Kr and Xe respectively. The experiments were carried out using a pulsed Fourier-transform-limited narrow-band UV laser and a supersonic-beam apparatus.

The fine and hyperfine structures of *n*p and *n*f Rydberg states of the nine and six natural isotopes of xenon and krypton, respectively have been analyzed in the range of principal quantum number *n* between 60 and 75 using multichannel quantum-defect-theory (MQDT). For the analysis of the fine and hyperfine structure we followed the formalism introduced for the $\mathrm{I} = 0$ isotopes by Lu and Lee [1] and Lu [2] and its extension in our group [3, 4, 5, 6] to treat the hyperfine structure in ^{83}Kr, ^{129}Xe and ^{131}Xe. Improved values of the ionization energies, the isotopic shifts and hyperfine coupling constants of $^{83}\mathrm{Kr}^+$, $^{129}\mathrm{Xe}^+$ and $^{131}\mathrm{Xe}^+$ were derived from the MQDT analysis.

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Radiative and tunneling decay dynamics in the $A\,^3\Sigma_u^+ - C\,^3\Sigma_g^+$ system of He_2

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He_2 is a four-electron molecule and a prototypical example of a Rydberg molecule [1]. Its electronic ground state ($X\,^1\Sigma_g^+$) only sustains one rovibrational level [2] and most spectroscopic studies are carried out from the metastable a $^3\Sigma_u^+$ state (see e.g., [3, 4, 5]). Several electronically excited states of He_2 have potential energy functions exhibiting local maxima leading to complex radiative and tunneling dynamics, the $c\,^3\Sigma_g^+$ state being a characteristic example [6].

We report on an investigation of the radiative and tunneling decay processes of the $c\,^3\Sigma_g^+$ state of $^4He_2$. To probe the dynamics in this state, we use a variety of pump-probe detection schemes including

$$(i)\quad He_2\ a(v'',J'')\ \xrightarrow{h\nu_1}\ c(v',J')\ \xrightarrow{-h\nu_2}\ a(v,J)\ \xrightarrow{h\nu_3}\ {He_2}^+\ X^+(v^+,J^+) + e^-$$

$$(ii)\quad He_2\ a(v'',J'')\ \xrightarrow{h\nu_1}\ c(v',J')\ \xrightarrow{h\nu_2}\ {He_2}^+\ X^+(v^+,J^+) + e^-$$

$$(iii)\quad He_2\ a(v'',J'')\ \xrightarrow{h\nu_1}\ c(v',J')\ \longrightarrow\ He^* + He\ \xrightarrow{h\nu_2}\ He^+ + e^- + He$$

These detection schemes in combination with the theoretical modelling of the relevant processes enable us to characterize the branching ratios of the competing tunneling and spin-rovibrational absorption/emission processes. The goal of these studies is to characterize the state-to-state decay dynamics in this fundamental molecular system by high-resolution spectroscopy

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Collisional parameters of $R(0)$ transition of CO in N_2

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The spectrum of the carbon monoxide molecule perturbed by other molecules is of great applied interest for Earth atmosphere sensing, as well as for the studies of various objects in the solar system. We present results of rigorous study of the first pure rotational transition of carbon monoxide perturbed by N_2. Measurements were carried out using two different by principle of operation spectrometers with complementary abilities covering together pressure range from 0.1 up to 1500 Torr and temperature range from 240 to 350 K. Low-pressure measurements made with the radioacoustic spectrometer are focused on the speed-dependent pressure broadening and shifting of the studied line and their temperature dependencies. The measured parameters are in a fair agreement with the results of the quantum scattering calculations based on the *ab initio* CO–N_2 potentials [1]. High-pressure measurements made with the resonator spectrometer, in addition, allow observation of the more subtle effects: the collisional coupling and the continuum absorption observed in this range as a pedestal proportional to the squared frequency.

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Chirality in tetraethyllead induced from an achiral structure through non-covalent interactions

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The high-resolution spectroscopic characterization of heavy-atom-containing molecules in the gas phase is highly intriguing due to various factors, such as the enhanced relativistic effects and parity-violating effects on the heavy atom. Featuring lead as the heaviest stable element, in this study, we investigated a van der Waals complex of a lead-containing compound, tetraethyllead (TEL), with 2-(trifluoromethyl)oxirane (TFO) using both microwave spectroscopy and quantum-chemical calculations. The monomer of tetraethyllead exhibits a D_{2d} molecular symmetry, thus is non-polar and achiral. With the presence of the chiral TFO, the TEL-TFO dimer as a whole becomes polar and the TEL moiety is transformed to a chiral arrangement under the non-covalent i nteractions. Among 75 nearly isoenergetic isomers (within 1.0 kJ/mol) predicted at the B3LYP-D4/def2-QZVP level of theory, only one configuration was observed and unambiguously assigned in the rotational spectrum. The assigned geometry is supported by its three Pb singly substituted isotopologues (^{206}Pb: 24.1%, ^{207}Pb: 22.1%, and ^{208}Pb: 52.4%), and further by the observation of the TEL-TFO-Ne trimer with its six doubly substituted isotopologues (^{206}Pb/^{207}Pb/^{208}Pb-^{20}Ne/^{22}Ne).

Investigation on THz solid state sources — evaluation for spectroscopic use

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The THz domain is increasingly used because calculating spectroscopic parameters in rotational spectra is easier than in ro-vibrational spectra. THz spectroscopy is increasingly used for atmospheric and astrophysical applications [1, 2]. This poster presentation explores the characterization of a solid-state sources for application in spectroscopy by analyzing its instrumental line shape (ILS), spatial beam homogeneity, power stability, and degradation due to amplitude modulation. The simulated line-shape tests performed allow for a better understanding of the source's behavior under different circumstances. The aim of this study was to characterize these aspects for quantitative spectroscopy applications. Some characteristics are available in the literature (power, power stability [3]), while others, such as spectral purity, are available [3], but not under the conditions usually used for spectroscopy studies. Some are absent, such as the beam spectral homogeneity and the modulation effect. The first step of this work was to confirm some results under conditions commonly used in spectroscopic studies.

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A true Omega representation as an adiabatic transformation of spin-orbit interactions and their associated non-adiabatic couplings

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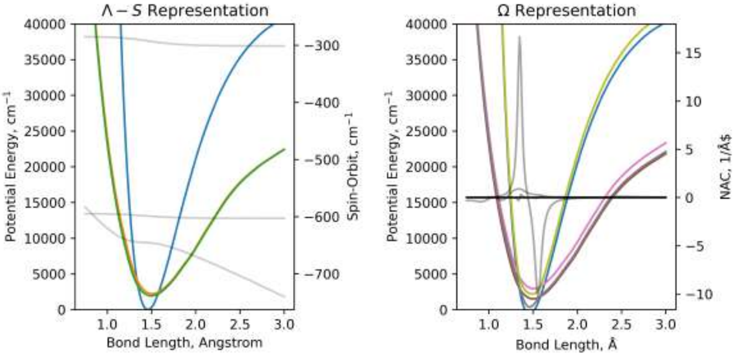
Removal of Spin-Orbit couplings (SO) for diatomic systems is a well established method which is thought to reduce the complexity of the system of study. This is done via diagonalisation of the associated Hamiltonian matrix with potential energy curves (PECs), transforming from the coupled $\Lambda - S$ (diabatic) basis to the Ω (adiabatic) representation where SO couplings vanish. This Ω–representation is thought to reduce the diatomic system to a desirable single state problem, which is simpler to treat and allows effective dipole moments to be computed for dipole-forbidden transitions. However, transforming to the Ω–representation does not completely decouple the system, in fact, strong non-adiabatic couplings (NACs) are introduced upon transformation of the kinetic energy, often ignored, and should be included. We show on selected diatomic systems that removal of SOC is not free, and omission of these "spin-orbit induced" NACs leads to gross errors into the rovibronic solution, unsuitable for high resolution spectroscopy, and a numerical equivalence between the $\Lambda - S$ diabatic representation and Ω– adiabatic representation is achieved when all NAC terms are included. This is true for any unitary transformation on the diatomic Hamiltonian, *nothing is achieved for free and simplification of one part leads to the complication of another*.



Heterodyne-based high-resolution THz spectroscopy on the AILES beamline of SOLEIL synchrotron and precision millimeter-wave spectroscopy of radical species

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Spectroscopic data for gas phase molecules in the THz domain (1-10 THz) are of significant interest for molecular physics laboratory astrophysics [1] and atmosphere physics [2]. However, due to the lack of powerful and tunable sources in this domain [3], spectroscopic measurements remain scarce. Through its large spectral coverage, high power and low noise THz radiation, synchrotron and especially the AILES beamline of SOLEIL synchrotron [4], are among the most suitable THz sources for spectroscopic applications. Nevertheless, commonplace Fourier transform spectrometers, used with such incoherent sources, limit the spectral resolution to tens of MHz. This resolution, larger than the Doppler broadening at room temperature, led us to develop a new THz high-resolution spectrometer [5]. Based on the heterodyne mixing of the THz continuum extracted by the AILES beamline with the laser lines produced by a QCL-based optically pumped molecular laser [6] acting as the THz local oscillator, this HR-spectrometer already provided some promising results [5] on stable species. In the present work, we associated it with a pulsed discharge to study radical species. Encouraging results and significant progress have been obtained: several NH_2 rotational transitions have been studied and structures previously unresolved have been revealed. To go beyond the Doppler resolution, and unveiled even more the hyperfine structure of radical species in the THz, further developments are required. However, sub-Doppler measurements have already been carried on NH_2 and ND_2 in the submillimeter-wave range (0.4 - 0.9 THz) and will be presented.

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Correlated rotational alignment spectroscopy and structure of benzene

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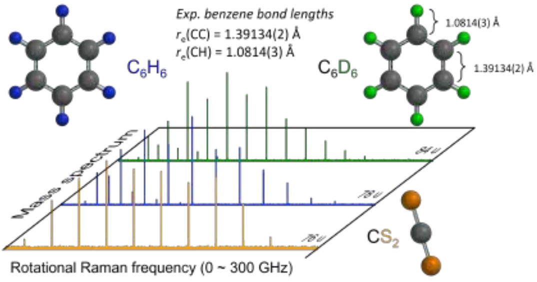
Mass-correlated Rotational Alignment Spectroscopy, mass-CRASY, combines the high sensitivity of mass spectrometry with high-resolution rotational spectroscopy. The mass selectivity of CRASY allows to distinguish isotopologue signals at natural abundance. The CRASY experiment is based on a pump-probe laser excitation scheme. The pump pulse created rotational wave-packet through rotational Raman transitions. The probe pulse ionized the molecules. Cation signals were recorded as function of an interferometric time-delay between the two pulses. Rotational Raman spectra were obtained by Fourier-transformation of time dependent signal modulations.

A mechanical delay stage and the pulse-selection of oscillator pulses allowed us to measure pump-probe signal with an effectively infinite interferometer range. This removed the dominant resolution limit for interferometric measurements and allowed us to obtain the world's highest resolution in the field of scanned interferometric spectroscopy (sub-kHz).

We measured data for a benzene sample, containing C_6H_6 and C_6D_6, and obtained rotational Raman spectra for both molecules (see figure below) and for their ^{13}C isotopologues. The data was used for an experimental structure determination. Equilibrium (r_e) and effective (r_0) bond lengths were estimated from our measured set of isotopologue rotational constants and from literature constants. The estimation of r_e was based on Watson's rovibrational correction terms. The determined benzene structure contradicted preceding experimental parameters derived from rotational spectroscopy but was in excellent agreement to theoretical and semi-experimental results.



Correlating parent-fragment relationships in CS_2 cluster photoionization

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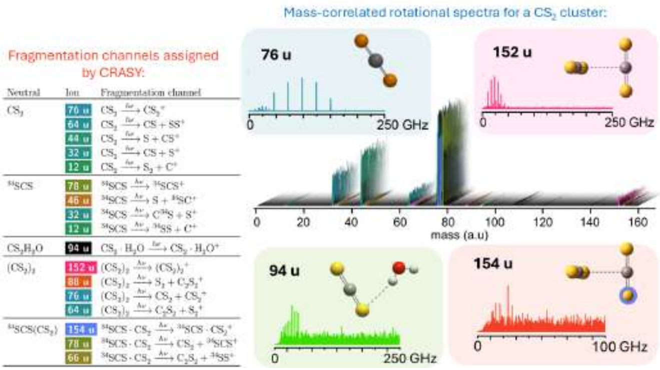
Almost all molecular samples encountered in our world are heterogeneous. When investigating such samples using traditional spectroscopy methods, we cannot distinguish which signal originates from which molecule.

Correlated Rotational Alignment Spectroscopy (CRASY) offers a solution to identify the origin of signals by correlating high-resolution rotational Raman spectroscopy with mass spectrometry. This approach allows the characterization of molecular composition and structure in impure molecular samples. Here, we present CRASY data for CS_2 clusters, as shown in the figure. The mass spectrum, accompanied by a mass-correlated pump-probe time trace scanned for 50 ns (equivalent to 17 MHz FWHM), and their Fourier-transformed rotational Raman spectra (0–250 GHz) were analyzed. Since the rotational wavepacket is excited and probed before photoionization, signals originating from the same parent molecule exhibit identical rotational spectra.

In this work, we characterized 8 distinct CS_2 isotopologues, 3 distinct CS_2 clusters, 13 distinct fragments, and 1 unexpected impurity. We successfully assigned 32 distinct ionization and fragmentation channels for the CS_2 cluster based on their mass-correlated rotational fingerprints.



Fragmentation channels assigned by CRASY:

Neutral	Ion	Fragmentation channel
CS_2	76 u	$CS_2 \xrightarrow{h\nu} CS_2^+$
	64 u	$CS_2 \xrightarrow{h\nu} CS + SS^+$
	44 u	$CS_2 \xrightarrow{h\nu} S + CS^+$
	32 u	$CS_2 \xrightarrow{h\nu} CS + S^+$
	12 u	$CS_2 \xrightarrow{h\nu} S_2 + C^+$
^{34}SCS	78 u	$^{34}SCS \xrightarrow{h\nu} {}^{34}SCS^+$
	46 u	$^{34}SCS \xrightarrow{h\nu} S + {}^{34}SC^+$
	32 u	$^{34}SCS \xrightarrow{h\nu} C^{34}S + S^+$
	12 u	$^{34}SCS \xrightarrow{h\nu} {}^{34}SS + C^+$
CS_2H_2O	94 u	$CS_2 \cdot H_2O \xrightarrow{h\nu} CS_2 \cdot H_2O^+$
$(CS_2)_2$	152 u	$(CS_2)_2 \xrightarrow{h\nu} (CS_2)_2^+$
	88 u	$(CS_2)_2 \xrightarrow{h\nu} S_2 + C_2S_2^+$
	76 u	$(CS_2)_2 \xrightarrow{h\nu} CS_2 + CS_2^+$
	64 u	$(CS_2)_2 \xrightarrow{h\nu} C_2S_2 + S_2^+$
$^{34}SCS(CS_2)$	154 u	$^{34}SCS \cdot CS_2 \xrightarrow{h\nu} {}^{34}SCS \cdot CS_2^+$
	78 u	$^{34}SCS \cdot CS_2 \xrightarrow{h\nu} CS_2 + {}^{34}SCS^+$
	66 u	$^{34}SCS \cdot CS_2 \xrightarrow{h\nu} C_2S_2 + {}^{34}SS^+$

Characterization and photochemistry of XCO_2 (X = F, NH_2, CH_3) radicals

S. Kechoindi[1] **, *S. Ben Yaghlane*[1] , *N. Terzi*[1] , *J. Palaudoux*[2] , *M. Hochlaf*[3]**

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The XCO_2 (X = F, NH_2, CH_3) radicals are present in the Earth atmosphere, where they are produced by the degradation of Volatile Organic Compounds (VOCs), either industrial or natural [1]. Here, we use advanced ab initio methodologies to characterize these species in their ground and electronically excited states. Computations are carried out using the Coupled Clusters, both standard and explicitly correlated versions, and multiconfigurational approches. Several basis sets were used. Afterward, the geometrical parameters and the total energies were extrapolated to the complete basis set (CBS) limit. We also mapped their potentials along the central bond to have insights on the $XCO_2 \longrightarrow X + CO_2$ reactions. We thus show that the ground and the lowest electronic excited states are long-lived, for which we provide a set of accurate structural and spectroscopic parameters. The upper electronic states are subject of unimolecular decompositions producing CO_2 and X fragments. Our calculations show that the FCO_2 (X^2B_2) $\longrightarrow$F(^2P) + CO_2 ($X^1\Sigma_g^+$) and the CH_3CO_2 (X^2A'') $\longrightarrow$ CH_3 (X^2A_2'') + CO_2 ($X^1\Sigma_g^+$) processes require at least 3.5 eV energy to occur, while less energy (of $\sim$ 2.5 eV) is needed for the NH_2CO_2 (X^2A'') $\longrightarrow$ NH_2 (X^2B_1) + CO_2 ($X^1\Sigma_g^+$) reaction. The present finding and data are useful to characterize these radicals in the laboratory, in planetary atmospheres and in combustion and to understand their physical chemistry there.

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Contributed speaker ThB1
Thursday 5 September, 14:00
Chair: G. Fuchs
Room B
Astronomy and atmospheres

Photochemical properties of astrochemically-relevant silicon clusters: bridging the gap between diatomics and silicate grains

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Interstellar dust is part of the universal recycling process of matter. A major component of interstellar dust are silicon carbides, silicon oxides, and metal-containing silicates, as inferred from IR emission and the detection of grains in meteorites. On the other hand, small silicon-containing molecules (<10 atoms) have firmly been detected in circumstellar shells by radio astronomy. Linking these two size limits from small molecules to micron-sized grains is a long-standing and still open issue. Although some hypotheses assume nucleation of seed particles, details of the growth mechanism(s), potential intermediates, and the impact of physical parameters such as radiation field, temperature, and chemical composition, remain largely unexplored. To shed further light on the nucleation process from the laboratory point of view, we investigate physical and chemical properties of small to medium-sized silicon carbide and silicon oxide clusters as a function of composition and charge state. To this end, the clusters are produced by laser vaporization techniques of various targets in molecular beams and probed by mass spectrometry, laser spectroscopy, and quantum chemistry. In a first step, geometric structures and chemical bonding of the clusters in the ground electronic state are obtained by IR spectroscopy using photodissociation and photoionization schemes, along with global optimization techniques in quantum chemical calculations. In a second step, optical and photochemical properties are obtained by UV-VIS photodissociation spectroscopy, providing important information about electronic structure and fragmentation properties (appearance energies, competing fragmentation channels and branching ratios, particularly stable fragments). Results will be presented for selected silicon carbide and oxide clusters.

Temperature-dependent photodissociation cross sections and rates for H_2S

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The photodissociation of molecules impacts the composition and dynamics of many astronomical systems. The vacuum ultraviolet (VUV) irradiation of hot Jupiters by their host star leads to complex photochemistry in their upper atmosphere. In the study of observable exoplanets and other hot astronomical bodies, it is thus critical to understand the effect of temperature ($T > 1000$ K) on such processes. Due to increased interest in sulfur chemistry with recent James Webb Space Telescope (JWST) detections of SO_2, H_2S photodissociation is of particular importance. H_2S is the primary equilibrium sulfur species in the lower atmosphere of exoplanets and is expected to yield S, HS, S_2, SO and SO_2 as subsequent photochemical products in their upper atmosphere [1]. This work presents preliminary temperature-dependent H_2S photodissociation cross sections and rates in the 160 – 240 nm (41667 – 62500 cm^{-1}) spectral region. All triatomic nuclear motion calculations were performed with an exact kinetic energy operator in the EVEREST computational suite [2] using *ab initio* potential energy and transition dipole moment surfaces from Chen *et al.* [3]. These data are compared to experimental measurements at room temperature from Lee *et al.* [4] and photodissociation rates are calculated for several radiation fields.

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Discovery of a new electronic state in iron hydride assigned to $(2)^4\Phi$

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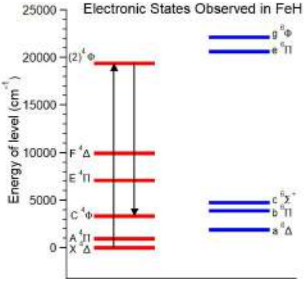
Iron Hydride (FeH) is a magnetically responsive diatomic molecule found in sunspots and cool K-M class stars and hence is of interest to astronomers. Transitions due to FeH are included in analysis of stellar spectra to measure the radial velocity of a star, its magnetic field strength, and to detect exoplanets in orbit around the star. Using laser excitation spectroscopy and dispersed fluorescence we have discovered a new FeH electronic state which we have assigned as $(2)^4\Phi$ at 19414 cm^{-1}. The last FeH electronic states to be identified 20 years ago were the $E^4\Pi$ and $A^4\Pi$ states [1] in the quartet manifold (see figure). We excited the $(2)^4\Phi$ state from $X^4\Delta$ with green laser radiation and measured very strong red fluorescence to $C^4\Phi$. This is the first electronic state in the quartet spin manifold discovered above 10000 cm^{-1} and can be used to access/study lower quartet states like the astrophysically significant $E^4\Pi$ and $A^4\Pi$ states [2]. Additionally, we performed a literature review of FeH and have used the MARVEL software package [3] to determine the best possible term values for of its currently observed energy levels in a global study.



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Rotationally resolved PFI-ZEKE photoelectron spectroscopy of the CH_3 radical probing the $X^+\ {}^1A_1'$ ($\nu_2{}^+ = 1$ and $\nu_4{}^+ = 1$) levels of the $CH_3{}^+$ cation

***N. Chen*[1] *, H. Le*[1] *, B. Gans*[1] *, S. Boyé-Péronne*[1] *, P. B. Changala*[2] *,* <u>*C. Alcaraz*</u>[3]**

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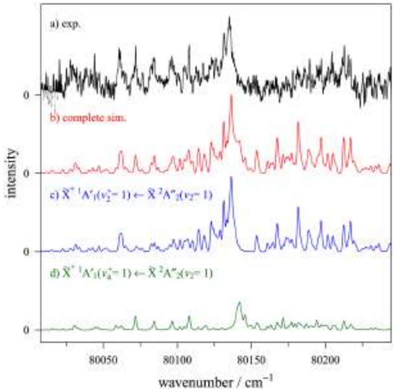
A lot of experimental efforts have been put in the last decades at UPSaclay on the study of the spectroscopy and reactivity of $CH_3{}^+$ cations [1] which started with the development of sources of CH_3 radicals and their adaptation to synchrotron or laser sources. The recent rotationally resolved PFI-ZEKE study with a high resolution VUV laser presented here is a striking result of such a continuous work as it helps to confirm [1] the first direct observation of the $CH_3{}^+$ cation (by emission at 7 µm) in a protoplanetary disk by the JWST telescope [2]. High-level quantum-chemical calculations that accurately account for the strong Coriolis interactions beetween the out-of-plane $\nu_2{}^+$ and in-plane $\nu_4{}^+$ bending modes have been crucial for the understanding of the rovibronic structure of $CH_3{}^+$ and thus to model the experimental spectrum.



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Photoelectron spectroscopy of small free radicals at medium- and high-spectral resolution

N. Chen[1] ***, H. Le***[1] ***, S. Boyé-Péronne***[1] ***, B. Gans***[1]

[1] Institut des Sciences Moléculaires d'Orsay (ISMO), 598 Rue André Rivière, 91400 Orsay (France)

More than 30% of molecules detected in space are free radicals or their ions [1], and they are also important intermediates in many chemical reactions. However, studying these species in the laboratory is challenging due to their high reactivity. Photoionization spectroscopy in the vacuum ultraviolet (VUV, 6-20 eV) range is a powerful tool for investigating the cationic states of free radicals. Compared to microwave or infrared spectroscopy applied to ions, this technique offers several advantages, such as avoiding the concentration loss due to the electrostatic repulsion among cations. The development of bright and narrow VUV radiation sources, such as the high-resolution VUV laser of the VULCAIM (VUv Laser for Considering Astrophysical and Isolated Molecules) [2] set-up at ISMO, and the broadly tunable VUV synchrotron radiation at the DESIRS beamline of the SOLEIL synchrotron [3], enables new photoionization measurements. During my thesis, I coupled various radical sources (pyrolysis, electric discharge, and chemical reaction) to photoionization spectrometers under VUV radiation, aiming to produce *in situ* free radicals molecules in an abundant and controlled way and to study their cationic states using photoionization spectroscopy.

Using pyrolysis and electric discharge coupled with VULCAIM, radicals such as CH_x (x=1-3) and NH_y (y=1,2) were generated from suitable precursors, and high-resolution photoelectron spectra (PFI-ZEKE) were obtained for vibrationally hot CH_3 radicals [4]. In a fluorine flow-tube reactor, coupled with the double-imaging photoelectron/photoion coincidence (i^2PEPICO) spectrometer at SOLEIL, a series of $Si_xC_yH_z$ radicals were generated using the precursor SiH_4/CH_4, offering essential insights into the vibronic structure of their cations.

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Stellar wind contribution to origin and transport of water on the surface of oxygen-containing minerals, Part I

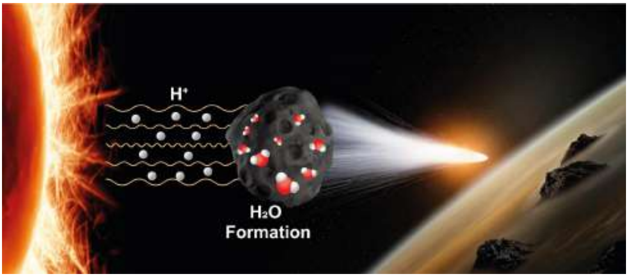
S. Civiš[1] **, *J. Kubišta***[1] **, *J. Plšek***[1] **, *A. Knížek***[1]

[1]J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, CZ18223, Prague (Czech Republic)

Liquid water covers more than 70% of the Earth's surface and more water is present in the Earth's interior. The origin of water on Earth is a hotly debated topic with many suggesting that the majority of Earth's water was brought in by water-rich asteroids and comets.

Alternatively, stellar wind irradiation of oxygen-containing minerals results in a reaction between H ions and the minerals to produce water and OH. We used high-resolution Fourier transform infrared spectroscopy and temperature programmed desorption with mass detection to observe water formation on the surfaces of 14 oxygen-bearing minerals in the laboratory. The formed water remains adsorbed on the mineral surface at pressure as low as 10^{-9} mbar and temperature as high as 600 K, which opens a possibility for transport over long distances and timescales in the Universe.

This process could explain the presence of water in the regoliths of airless worlds such as the Moon, or on the surfaces asteroids and comets.



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Stellar wind contribution to origin and transport of water on the surface of oxygen-containing minerals, Part II

S. Civiš[1] **,** ***J. Kubišta***[1] **,** ***J. Plšek***[1] **,** ***A. Knížek***[1]

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The experiments with the formation of water on the surface of oxygen-containing minerals were described in Part I. Using the estimated amount of water in the Earth's hydrosphere and the adsorption capacity of minerals obtained from our experiments, the mass of material required to deliver that amount of water was calculated and the result is shown in the Table.

To explain the origin of one ocean equivalent of Earth's water by impact delivery of those minerals from space, one would require $10^{19} - 10^{20}$ kg of delivered mass, which is comparable to the 10^{20} kg of material delivered during the Late heavy bombardment. This suggests that solar wind might have been a significant source of water on Earth.

Sample	**Ads. Capacity (wt.%)**	**mtot (kg)**
Fe_2O_3	0.158	9.24×10^{19}
TiO_2-P25 anatase	0.262	5.57×10^{19}
Montmorillonite	0.152	9.61×10^{19}
Kaolinite	0.147	9.93×10^{19}
Augite	0.120	1.68×10^{19}
Diallage	0.685	3.30×10^{19}
Oligoclase	0.094	1.22×10^{20}
Al_2O_3	0.288	2.13×10^{19}
Olivine	0.148	1.55×10^{20}
RaS 445 meteorite	0.461	5.07×10^{19}
SaU 567 meteorite	0.154	3.17×10^{19}
TiO_2 nanorutile	0.442	9.86×10^{19}
TiO_2 anatase	0.087	9.48×10^{20}

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Contributed speaker ThC1
Thursday 5 September, 14:00
Chair: H. L. V. Nguyen
Room C
Non covalent interactions

Molecular beam microwave spectroscopy: large amplitude motions and non-covalent bonds

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Structure of ice and solid H_2S when it freezes led Pauling [1] to conclude that H_2O has hydrogen bonding and H_2S has van der Waals interactions, though there was no fundamental understanding of what these two terms meant, leading to a lot of debate and controversies in the last century. Spectroscopy of weakly bound complexes formed in a molecular beam or cold matrix have helped enormously in our understanding of weak non-covalent bonding. It started with the observation of the hydrogen bonded HF dimer by molecular beam electric resonance (MBER) in 1972 [2]. In 1975, matrix isolation technique was used to study the lithium bonded $FLi \cdots NH_3$ [3]. The next year, MBER technique was used to identify $HF \cdots ClF$ complex [4], which was then characterized as anti-hydrogen bonded and now recognized as the first halogen bonded complex to be investigated by spectroscopy. The development of molecular beam microwave spectroscopy by Flygare [5] and that of the chirped-pulse microwave spectrometer by Pate [6] have revolutionized investigations on weakly bound complexes formed in a supersonic beam typically at 2-3 K. In parallel, crystallographic investigations in solids and ab initio theoretical investigations have led to the characterization of intermolecular non-covalent bonds formed by every element in the main groups of the periodic table. We have shown that H_2S dimer is hydrogen bonded [7] and $CH_3CN \cdots CO_2$ is carbon/tetrel bonded [8] in recent years. In 2009, we proposed that the barrier for large amplitude tunneling motions which can break a hydrogen bond should be below the zero-point energy along the corresponding vibrational coordinate [9] in order to be characterized so. This talk will give a summary of the spectroscopic developments in the last five decades which have helped in our understanding of intermolecular non-covalent bonds.

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Rotational spectroscopic study of the PA-FA-PHS complex

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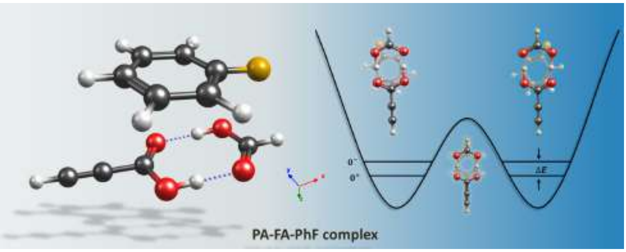
Proton tunneling plays a crucial role in various biological processes. It not only influences DNA replication by causing mis-pairing of bases, potentially leading to mutations, but also facilitates proton transport in proteins and enhances the catalytic efficiency of enzymes. Therefore, research into the mechanisms of proton tunneling is of great significance. Microwave spectroscopy is a powerful tool for studying molecular structures and large amplitude motions. Herein, we report the rotational spectra of the propiolic acid-formic acid dimer (PA-FA) complexed with fluorobenzene (PhF) within the frequency range of 2 to 8 GHz. The spectrum exhibits a splitting pattern, with both *a*- and *b*-type transitions splitting into two components, indicating the concerted double proton transfer tunneling in the hydrogen bonds of carboxylic acid dimer. The structure of PA-FA-PhF was assigned to be π-π stacking. The energy splitting between 0^+ and 0^- states decreases compared to the PA-FA dimer.



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Interactions of a ketone with a higher number of waters in the gas phase: structures and binding preferences of cyclooctanone$\cdots$(H_2O)$_{3-8}$ clusters

V. Tsoi[1] **, *E. Burevschi***[1] **, *M. E. Sanz***[1]

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Understanding the first interaction stages of water with organic molecules is of great interest given the ubiquity of water in nature. Here we explore the microsolvation of the eight-membered cyclic ketone cyclooctanone (CYO) using chirped pulse Fourier transform microwave spectroscopy. We previously assigned three conformers of CYO monomer and four complexes of CYO$\cdots$(H_2O)$_{1,2}$ [1, 2]. Cyclooctanone hydrates with higher number of water molecules, CYO$\cdots$(H_2O)$_{3-8}$, have now been observed and identified with the aid of *ab initio* and DFT methods. Most of the complexes show several arrangements, highlighting the versatility of water molecules in their interactions with an organic solute. The trends of the complexes' binding preferences and relevant interactions will be discussed and compared.

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Configurations of *o*-phthalaldehyde–$(H_2O)_{1-3}$ complexes elucidated by rotational spectroscopy

V. Tsoi[1] ***, M. E. Sanz*** [1]

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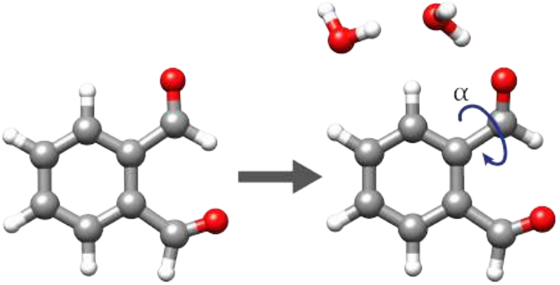
Investigation of the clusters of aerosol precursors with atmospheric molecules provides insight into the initial stages of aerosol nucleation. *o*-phthalaldehyde (OPA), formed by a benzyl ring with two aldehyde groups substituted in the ortho position, is an oxidation product of naphthlene and has been classified as a precursor of secondary organic aerosol. We have studied the interactions of OPA and water, one of the most common molecules in the atmosphere, using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy with the support of *ab initio* and DFT calculations. The lowest-energy conformer of OPA was previously characterised using Fabry-Pérot FTMW spectroscopy, X-ray crystallography, and NMR spectroscopy [1]. We have identified a higher-energy conformer of OPA, as well as various isomers of the mono-, di-, and trihydrates of OPA. We will discuss the observed conformational preferences, preferred binding sites and relevant interactions, as well as changes in the structure of OPA induced by water.



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Rotational spectroscopy and tautomeric equilibria in complexes formation of benzisothiazolinone

J. Li[1] **, *D. Loru***[1] **, *W. Sun***[1] **, *M. Schnell***[1]

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Solvent properties, such as polarity and proticity, play a significant role in influencing tautomeric equilibria, leading to shifts in preference towards different tautomeric forms [1]. As it is structurally related to isothiazolinone, whose NH-form predominates in more polar and protic solvent, benzisothiazolinone (BIT) also possesses a tautomeric intramolecular equilibrium between the NH-form and the OH-form, which has not been reported in the gas phase so far [2, 3]. In our current study, we used CREST, the conformer-rotamer ensemble sampling tool [4], along with geometry optimization at the B3LYP-D3(BJ)/def2-TZVP level of theory to investigate the tautomeric conformations of BIT complexes with water and formic acid, respectively. Rotational spectra of BIT-water or formic acid adducts were recorded in the 2-8 GHz range by using a chirped-pulse Fourier transform microwave spectrometer and analyzed. Pure rotational transitions were assigned to several tautomers of BIT$-$(H_2O)$_{1,2,3}$ and BIT$-$(HCOOH)$_{1,2}$, respectively. The relationships between the geometries of the observed structures, the non-covalent interactions and the tautomeric equilibria of the two mentioned molecular systems will be discussed.

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Rotation visualizing solvation: studying oligo hydrates of 4-hydroxy-2-butanone

M. Li[1] ***, J.-U. Grabow***[1] ***, W. Li***[2] ***, C. Pérez***[2] ***, A. Lesarri***[2]

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Structural changes induced by water play a pivotal role in chemistry and biology but remain challenging to predict, measure, and govern at the molecular level. A few mono-(water)$_n$ clusters [1, 2, 3, 4], where n = 0-5 or 0-6 have been studied to reveal the balance between structural deformation of the solute and water self-aggregation. In most cases, the water molecules in the clusters form self-association networks resembling the corresponding pure water clusters, being called droplet aggregation [1, 2, 4]. However, recent study on the 3-methylcatechol-$(H_2O)_{1-5}$ [3] proves that the structure of water molecules become visibly different from the pure water clusters, thus termed wetting pathway. Besides, for studies of rigid solutes, like benzaldehyde [4], indicate that the solute's degree of flexibility affects the balance between the solute's structural alteration and water self-aggregation in size-governed clusters.

A flexible molecule, 4-hydroxy-2-butanone (4H2B) features hydrophilic alcohol and carbonyl groups. The study of the 4H2B monomer and its monohydrates [5] shows minor structural changes upon the 4H2B moiety in the monohydrate relative to the free monomer. In this context, larger clusters, 4H2B-$(H_2O)_{2-5}$ have been investigated by broadband rotational spectroscopy [6, 7] rationalized with quantum chemical calculations. Interestingly, the structures of each 4H2B substrate in observed isomers of 4H2B-$(H_2O)_{2-5}$ undergo various alterations compared to the free monomer while the aggregation of water molecules in these clusters follows the droplet pathway.

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Microwave spectroscopic study of solvation processes in $\pi - \pi$ stacking

X. Chen[1] ***, G. Wang***[1] ***, X. Zeng***[1] ***, W. Li***[1] ***, M. Zhou***[1]

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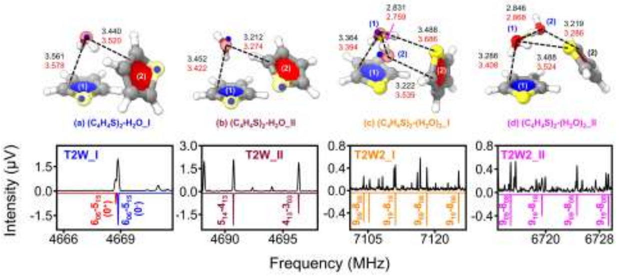
π-π interactions are widely prevalent in nature and play crucial roles in the structural maintenance and functionality of proteins. However, the effect of water on π-π stacking remains a contentious issue. Some theoretical studies suggest that water can accelerate the formation of π-π stacking, while other evidence indicates that water destabilizes π-π stacking. These conclusions are primarily based on theoretical calculations and lack experimental support. In this work, we investigated the thiophene-water system using high-resolution microwave spectroscopy and characterized the structures of various thiophene-water clusters. Among all the observed thiophene-water clusters, no π-π stacking was observed between thiophene dimer. Instead, due to the insertion of water, a novel V-shaped configuration was presented. This work experimentally demonstrates that water can exhibit a disruptive effect on π-π stacking.



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Contributed speaker ThD1

Thursday 5 September, 14:00
Chair: O. Pirali
Room D
Laser spectroscopy

Jet-cooled mid-infrared laser spectroscopy of centrosymmetric and N-bearing PAHs

P. Asselin[1] ***, S. Chawananon***[2] ***, O. Pirali***[2] ***, M. Goubet***[3]

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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 their formation and destruction pathways. In the mid-infrared (IR) domain, the launch of the James Webb Space Telescope opens exciting perspectives to collect rovibrational information about low volatile polycyclic aromatic compounds. In this context, rotationally resolved IR studies of large aromatic species are still very scarce and mainly used synchrotron-based Fourier Transform (FT) spectroscopy coupled to room temperature long path cells [2]. However, their spectral analysis remains very challenging due to the congested rotational structures and the presence of many hot bands. Nowadays, few set-ups combining high resolution (HR) IR spectroscopy to supersonic jets, using FT and cavity ring down spectroscopic methods were implemented to target PAH compounds [3, 4]. Recently, a mid-IR laser spectrometer coupled to a pulsed jet (SPIRALES set-up at MONARIS) allows recording rovibrational spectra of large molecules at low temperature [5]. We report here the jet-cooled rovibrational IR study of centrosymmetric PAH molecules in both regions of ring C-H bending and C-C stretching vibrations to extract reliable spectroscopic parameters both in ground and excited vibrational states [6]. HR measurements of N-bearing PAHs with up two N atoms substituted on the same ring evidenced abnormal Q-branch structures which make puzzling rovibrational analyses and suggests the presence of vibrational perturbations in spectral regions with high density of states.

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Far infrared absorption spectroscopy of the nine stable isotopologues of water vapor

S. N. Mikhailenko[1] **, A. O. Koroleva**[2] **, E. V. Karlovets**[3] **, A. Campargue**[3]

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The aim of the present work is to improve the knowledge of the absorption spectrum of all the stable isotopologues of water vapor in the far infrared (FIR), between 50 and 720 cm^{-1}. The considered FIR region corresponding to the rotational band of H_2O is of major importance for the Earth's radiation budget and for the Far-infrared-Outgoing-Radiation Understanding and Monitoring (FORUM) mission of European Space (https://www.forum-ee9.eu/).

In the fall of 2021, a one-week measurement campaign at the AILES beam line of the SOLEIL synchrotron was dedicated to FTS recordings of 21 high resolution spectra of various mixtures of water isotopologues (natural, ^{17}O and D enriched). The SOLEIL spectra recorded with a 151 m pathlength provided a gain in sensitivity by more than three orders of magnitude compared to previous studies. From the large amount of newly measured absorption lines, a significant number of new energy levels could be determined and valuable validation tests of the current spectroscopic databases could be performed. The analysis of the spectra of natural water [1], ^{17}O enriched water [2] and D_2O isotopologues [3] have been completed and will be summarized. Current progress in the analysis of the spectra of the HDO species will be presented.

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Experimental determination of the Landé g-factors for the $N = 1$ rotational energy levels in the ground vibronic state ($X^3\Sigma_g^-, v = 0$) of $^{16}O_2$

A.-W. Liu[1] **, Y.-R. Xu**[1] **, Z.-T. Zhang**[1] **, Y.-Q. Cheng**[1] **, Y. Tan**[1] **, S.-M. Hu**[1]

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Experimentally determining the Landé g-factor of the rotational energy states in the oxygen vibronic state ($X^3\Sigma_g^-, v = 0$) has long been a challenge. Saturated absorption spectroscopy (SAS) of rovibrational transitions in the A or B band of oxygen are better candidates for the experimental measurement of the Landé g-factors since the upper singlet electronic state $b^1\Sigma_g^+$ is independent of the Zeeman effect. High-resolution SAS of the $^PP(1)$ and $^RQ(2)$ transitions in the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-(0,0)$ band of $^{16}O_2$ have been measured with a comb-locked cavity ring-down spectrometer under uniform magnetic fields ($B \leq 2.5$ Gauss). The parallel alignment of the laser beam and the magnetic field allows for significantly higher precision in measuring the $\sigma_\pm$ Zeeman components compared to the experiment conducted under the geomagnetic field [1]. The centers of $M = \pm J$ Zeeman components have been determined with an accuracy better than 5.0 kHz. This has allowed for the experimental determination of the Landé g-factors with a relative accuracy of better than 1% for the $N = 1$ rotational states. These results would be used not only to assess the Zeeman effect on atmospheric temperature remote sensing profiles at high altitudes [2], but also as a benchmark to test the spin-orbit coupling and related effects in the Hamiltonian model [3].

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Si-traceable density measurement of H_2 based on polarizability and absorption spectroscopy

S.-M. Hu[1] **, *H. Liang*[1] , *Z.-L. Nie*[1] , *J. Wang*[1] , *Y. Tan*[1] , *C.-L. Hu*[1] , *C.-F. Cheng*[1] , *A.-W. Liu*[1] , *Y. R. Sun*[2]**

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The hydrogen molecule is the simplest neutral molecule that can be calculated precisely with *ab initio* methods based on quantum electrodynamics (QED) theory and a few fundamental physical constants. Precision spectroscopy of the hydrogen molecule is an ideal testbed for full quantum calculations of few-body systems. In this work, we demonstrate two optical methods for SI-traceable determination of the molecular density of H_2: refractive index measurement and absorption spectroscopy. The electric dipole polarizability of the hydrogen molecule was determined to be 2.031027(71) $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ with a refractometer at 298 K, which agrees with the recent theoretical value [1] and considerably improves previous experimental results. Doppler-broadened spectra of the first overtone Q(1) line of the H_2 molecule near 1.2 μm were measured in the range of 20-80 kPa. Both absorption and dispersion spectra were recorded with a cavity-enhanced spectroscopy instrument [2] referenced to an optical frequency comb. Based on the Hartmann-Tran profile, the absorption and dispersion spectra were fitted independently. The line intensity was determined by the two methods with accuracy of 0.1%, agreeing well with the *ab inito* calculated result [3]. The present work demonstrates the potential of primary gas metrology based on optical measurements of hydrogen gas.

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Cavity ring-down spectroscopy of jet-cooled ethylene between 5880 and 6200 cm^{-1}

S. Perot[1] **, J. Lecomte**[1] **, N. Suas-David**[1] **, L. Rutkowski**[1] **, R. Georges**[1] **, M. Rey**[2] **, S. Kassi**[3]

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The high-temperature infrared fingerprint of ethylene (ethene, C_2H_4) is needed to detect its presence in the atmosphere of warm and hot Jupiter exoplanets. Nonetheless, the spectroscopic data for ethylene is very scarce, partly due to its 12 non-degenerate vibrational modes, leading to a highly congested spectrum, even at low temperatures.

In a first step, jet-cooled absorption spectra of ethylene were recorded at three different rotational temperatures (6/8 K, 12 K, 38 K) using cavity ring-down spectroscopy (CRDS) to expand the number of known cold band transitions in the 5880-6200 cm^{-1} spectral region. The rotational cooling enabled the identification of 320 rovibrational transitions in 20 interacting vibrational cold bands [1]. Among these 20 vibrational cold bands, 14 had never been observed before. The line by line assignments were performed by direct comparison with the TheoReTS variational line list [2] and a systematic use of lower state combination difference (LSCD). 15 of the identified bands could be fitted using PGOPHER [3] to precisely determine their band center.

In a second step, two spectra were recorded in the same spectral range by preheating the ethylene sample at 650 K and 850 K prior to its expansion through a Laval nozzle. This led to non-LTE (non-local thermodynamic equilibrium) conditions suitable for the recording of rotationally cold hot bands (SMAUG experimental setup [4, 5]). The identification of lines belonging to hot bands were performed on the basis of TheoReTS calculations, implementing our recently determined cold band centers. Hot-band assignments will be presented.

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High resolution dual frequency comb spectroscopy from 1 THz to 1 PHz

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Dual-comb spectroscopy across electromagnetic spectrum has evolved into a powerful technique that features simultaneously broad spectral coverage, high spectral resolution, and high speed, and is a spectroscopic method of choice for applications ranging from testing fundamental laws of science to pharmaceutical and chemical analysis, photochemistry, trace gas sensing, astronomical observations, and biomedical applications. I will present our results on extending the dual frequency comb spectroscopy both to the mid-IR-THz and to the visible and UV spectral regions. We start from two low-noise phase-locked frequency combs based on Kerr-lens mode-locked Cr:ZnS lasers with center wavelength 2.35μm and use three different techniques to explore spectral ranges at both longer and shorter waves. These include subharmonic optical parametric oscillation and optical rectification – for producing mid-IR-to-THz waves, and high harmonic generation – for the UV-visible generation. In the long-wave part of the spectrum, 1.5–45 THz (6.6–200μm), we combine the dual-frequency-comb spectroscopy with electro-optic sampling method of detection and are able to perform measurements with an instantaneous spectral coverage exceeding an octave (e.g., 7–16μm, 9-20μm, etc.). With the low noise of our dual-comb system we can capture a large amount of spectral information (up to 240,000 comb-mode-resolved spectral lines spaced by 80 MHz) in the mid-IR portion of the spectrum up to a video rate. This allowed high-resolution measurements with low-pressure gaseous ethanol, isoprene, and dimethyl sulfide and reveal Doppler-limited spectroscopic signatures that have never been explored before. To reach the UV-visible spectral range, we generate up to seventh-order harmonic of the Cr:ZnS laser output using multi-grating periodically poled lithium niobate (PPLN) crystal and reach UV wavelengths down to 326 nm (920 THz). The frequency comb produced via the 6th harmonic (370–410 nm) contains some million comb teeth resolved by the dual comb spectroscopy. High-resolution spectroscopic dual comb measurements in the UV will be also discussed. To the best of our knowledge, this is the first demonstration of dual-comb spectroscopy performed over such a wide spectral range, from THz to UV, in a single system with high resolution defined by the 80-MHz comb-mode spacing (which can be improved by a factor of 10^3 by interleaving the spectra taken with shifted combs), and with referencing to a rubidium atomic clock.

Spectroscopic study of a single molecule underneath the STM tip

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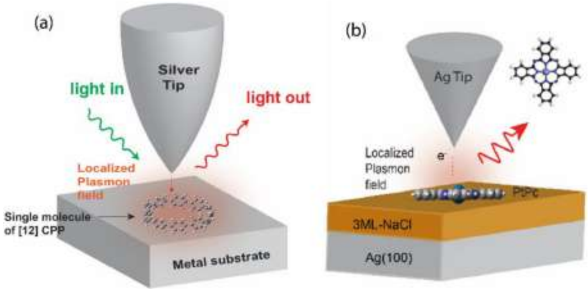
It is challenging to study the optoelectronic properties at the single molecule level due to optical diffraction limit in conventional spectroscopy. STM combined spectroscopy, tip-enhanced Raman scattering (TERS) and STM-induced luminescence (STML) techniques have been employed to investigate the chemical structural heterogeneity and electroluminescence of molecular systems. TERS, utilizing strong localized plasmonic field at the tip apex, provides enhanced vibrational signals. Most molecules studied under STM tip are planar π-conjugated systems lying flat on the surface [1, 2]. In this talk, I shall demonstrate TERS's capability to probe the structural information of standing-up π-conjugated cycloparaphylene molecules. These results offer comprehensive fundamental understanding of a single molecule vibration and open new avenues for plasmon-driven molecular vibrations. I shall also present the electroluminescence behavior standing-up π-conjugated molecular systems under the STML setup. STML is a precise approach to understand and control of a single-molecule luminescence mechanism [3]. I shall demonstrate the the stability of a single platinum phthalocyanine molecule at both bias polarities and discuss the complex electroluminescence behavior of a single molecule. The bipolar emission behavior results provide fundamental understanding of the excitation mechanism of single-molecule electroluminescence and pave the way for developing novel molecular optoelectronic devices.



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Invited Speaker FA

Friday 6 September, 9:00
Chair: M. E. Sanz
Room B

Magnetic resonance of biomolecules by combining ESR and NMR techniques

E. Bennati[1,2]

[1]Max Planck Institute for Multidisciplinary Science, [2]Institute of Physical Chemistry, University of Göttingen, Göttingen, Germany.

Latest developments in magnetic resonance spectroscopy use submillimetre wave instrumentation to polarize nuclear spins and increase sensitivity for nuclear spin detection, which is limited by the small energy splitting at available polarizing magnetic fields. A powerful approach is taking advantage of the larger magnetic moment of unpaired electrons and uses hyperfine couplings to transfer their polarization to magnetic nuclei.

The talk will illustrate recent progress in polarization transfer experiments either detecting the magnetic moment of unpaired electrons (ESR) or directly the nuclear spins (NMR). We have recently demonstrated that at electron Larmor frequencies around 300 GHz, nuclear chemical shift tensors as well as resonances of quadrupolar nuclei coupled to unpaired electrons can be resolved. In conjunction with ^{19}F spin labelling, our techniques can be employed for measuring inter-spin distances in biomolecules and gain structural information [1]. Moreover, we are developing dynamic nuclear polarization for enhanced NMR detection in the liquid state [2, 3, 4]. Progress and strategies for future applications will be discussed.

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Rotational insights into sulfur-mediated non-covalent interactions

G. Feng[1] ***, L. Wang***[1] ***, T. Yang***[1] ***, W. Lv***[1] ***, J. Huang***[1] ***, H. Huang***[1] ***, Y. Li***[1] ***,***
F. Shen[1] ***, Y. Feng***[1]

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The sulfur-mediated non-covalent interactions are of great significance for understanding the microscopic mechanisms of molecular recognition, binding and catalysis. We employed high-resolution Fourier transform microwave (FTMW) spectroscopy in combination with quantum chemical computations to characterize and understand the nature of these sulfur non-covalent interactions. In this contribution, we will present the structural and energetic details on several types of S non-covalent interactions including the chalcogen bonding, hydrogen bonding, and S-pi interactions. For this purpose, the model intermolecular complexes were investigated by pulsed jet Fourier transform microwave spectroscopy. The spectroscopic results are interpreted using quantum chemical calculations, natural bond orbital analysis, non-covalent interactions analysis, and Symmetry-Adapted Perturbation theory analysis to shed light on the non-covalent interactions at play.

Contributed speaker FB1

Friday 6 September, 11:00
Chair: S. Thorwirth
Room B
Astronomy and atmospheres

Searching for resonances states by complex scaling

T. Uhlíková[1] **, *S. Yurchenko***[2]

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Resonance states, as a special case of rovibronic metastable states, play crucial roles in radiative processes, although they often remain hidden within the dense forest of both bound and continuum states. Resonances can facilitate the creation of new molecules through radiative associations or the dissociation of systems at energies lower than their dissociation limits. Identifying these metastable states and characterizing their spectral properties, such as position and width, has posed a challenge for over a century. Various methods have been developed to address this challenge. One of them is complex scaling, also known as complex coordinates, coordinate rotation, or dilatation analyticity method [1].

The fundamental principle of complex scaling in identifying resonance states involves modifying the Hamiltonian in the Schrödinger equation by introducing a complex scaling parameter. Resonance states can be accurately calculated as eigenvalues of this modified Hamiltonian with complex eigenvalue energies,

$$E_n = \mathfrak{Re}(E_n) - \mathfrak{Im}(E_n) = \epsilon_n - (i/2)\Gamma_n,$$

where ϵ_n is the resonance position above the threshold, and Γ_n is the width (or inverse lifetime) of the resonance state.

In this study, the complex scaling method is employed to determine the resonance states of two different systems. The first system investigated is the dication $NO_2{}^+$, where every state is, in principle, metastable due to the repulsive potential of dications. Our theoretical predictions have recently been refined through kinetic energy release experiments [2]. Consequently, resonances are sought within the numerous spectral lines of NH radical photodissociation spectra. The findings from this research could offer new insights into the chemistry of atmospheres, the borders of dark clouds, stellar envelopes, and other environments where ultraviolet radiation, nitrogen, and hydrogen are present.

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Where experiment meets theory: the way to the new ExoMol line lists–LIV for AlH and AlD

W. Szajna[1]***, R. Hakalla***[1]***, S. N. Yurchenko***[2]***, J. Tennyson***[2]***, M. Semenov***[2]***, A. Sokolov***[2]***, R. R. Gamache***[3]***, Y. Pavlenko***[4]***, M. R. Schmidt***[5]***, R. W. Field***[6]

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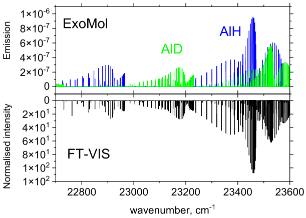
Recent FT-VIS measurements [1] and astrophysical findings [2] motivated the revision of the previous line lists for the aluminium hydride isotopologues. A new high-resolution emission spectra of the $A^1\Pi - X^1\Sigma^+$ cover eight bands $(0-0,1,2$ and $1-0,1,2,3)$ for AlH and ten bands $(0-0,1,2; 1-0,1,2,3$ and $2-1,2)$ for AlD. In total, 750 molecular lines have been measured with the accuracy of about 0.0020 cm^{-1}. The new line positions are combined with all available experimental data to construct a comprehensive set of empirical rovibronic energies of AlH and AlD covering the $A^1\Pi$ and $X^1\Sigma^+$ electronic states using the MARVEL approach. The extended experimental data were used to produce new high-temperature line lists which accurately represent the vibrational states of the shallow $A^1\Pi$ state: $v = 0, 1$ for AlH and $v = 0, 1, 2$ for AlD. The published line lists [3] are available via `www.exomol.com`.



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Towards accurate climate metrics by quantum chemical spectroscopic simulations

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Radiative efficiencies (REs) and global warming potentials (GWPs) are climate metrics that quantify the green-house capacity of atmospheric gases. As such, they are the indicators upon which decision makers propose new international regulations, plan mitigation actions and drive transitions in the production and consumption of chemicals used in different application fields. Besides the atmospheric irradiance profile, the infrared (IR) absorption cross spectrum is the fundamental quantity required to determine the RE of a molecule. A number of experimental challenges, however, has to be faced when aiming at achieving an accuracy of at least 5% in the measured absorption cross sections, this being particularly hampering for high-vapor pressure compounds. Computational spectroscopy can be exploited, especially in these situations, to compute the required spectral features to be used in place of the experimental data, provided that the main physical factors are taken into account in the simulations [1]. While computational methods have been used to estimate REs, their application has been limited to the use of double-harmonic approximation which presents serious limitations. In this contribution, a computational workflow to evaluate REs and GWPs of greenhouse gases is presented. The approach builds on (i) the non-empirical inclusion of both mechanical- and electrical-anharmoniciy, (ii) the evaluation of low-frequency contributions to the radiative properties, (iii) the consideration of conformational equilibrium. The computational approach is first validated against a training set of halogenated molecules, showing an accuracy on par with the most accurate experimental outcomes. The procedure is then applied to selected molecules: particular attention is given to HCFC-132b, recently detected in the atmosphere [2], for which experimental data was lacking.

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Theoretical vibrational analysis and Raman spectra of acetone isotopologues

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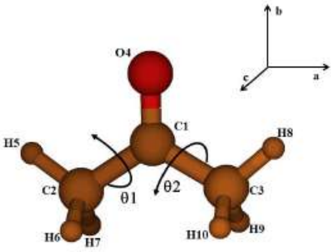
Acetone, one of the most significant ketones in the atmosphere, is produced in situ from various anthropogenic and natural volatile organic compounds (VOCs). We present the characterization of the vibrational spectrum of acetone and one deuterated isotopologue performed using explicitly correlated coupled cluster theory and a core-valence correlated consistent basis set. At this level of theory, rotational constants can be determined with a precision of a few MHz compared to the experimental data. The Raman spectra in supersonic gas jets, capable of probing molecular gas samples with high spatial and spectral resolution, has been recorded. The low temperature achieved in the jet significantly simplifies molecular spectra, thereby facilitating the assignment of the observed bands. Assignments are made with the help of calculations achieved using second-order perturbation theory and a reduced dimensionality variational procedure which considers the minimum interconversion. For acetone-h6, the torsional splitting of the ground torsional state (0,0,0) was evaluated to be $0.15\,\mathrm{cm}^{-1}$ [1].

The most intense band observed in the Raman spectrum, corresponds to the ν_7 C–C symmetric stretching and presents a complex structure at room temperature due to hot transitions from the first excited torsional level. Fermi resonances involving the fundamental displace the $(100) \rightarrow (101)$ transition to low frequencies.



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Machine learning estimate of the interstellar physical conditions from the observed spectral line profiles

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We have explored the effect of the interstellar physical conditions on the profiles of the molecular (sub)mm wave lines. This analysis has led us to use techniques of Machine Learning (ML) to estimate the physical conditions of the interstellar medium (ISM). Hence, we have simulated a comprehensive set of molecular spectral data at different ISM physical conditions, collecting the information of their profiles in the input variables used in ML approaches. ML algorithms have been trained and tested using these simulations and their results are compared with the observed spectral lines to estimate the physical conditions of the ISM source. In particular, we have considered, as an illustrative example, the spectral lines of the two isomers HCN and HNC because they were detected in many interstellar sources and have been proven suitable to determine the gas temperature and the evolution of an interstellar object [1, 2]. The joint analysis of the spectral lines of the two isomers HNC and HCN, using ML approaches, has permitted us to determine the relative abundance HNC/HCN and the excitation temperature of the APEX detections of these isomers towards the source RCrA IRS7B [3]. This work represents a new application of ML approaches in the field of molecular astronomy and astrochemistry [4, 5, 6].[17]

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[17] This project has received funding from the European Union's Horizon 2020 research and innovation program under Marie Sklodowska-Curie grant agreement No. 872081, grants PID2020-119478GB-I00 (A.P.) and PID2022-136228NB-C21 (M.C.) funded by MCIN/AEI/10.13039/501100011033, and, as appropriate, by "ERDF A way of making Europe", the "European Union", or the "European Union NextGenerationEU/PRTR".

Contributed speaker FC1

Friday 6 September, 11:00
Chair: A. Ross
Room C

Linelists and datasets

Multi-laboratory comparison of $^{12}C^{16}O$ $(3-0)$ line intensities: towards primary spectroscopic measurements of amount of gas

K. Bielska[1] , *V. D'Agostino*[1] , *S. Wójtewicz*[1] , *A. Cygan*[1] , *R. Ciuryło*[1] , *D. Lisak*[1] , *J. T. Hodges*[2] , *Z. D. Reed*[2] , *M. Birk*[3] , *G. Wagner*[3] , *C. Röske*[3] , *R. Guo*[4] , *G. Li*[5]

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Lines from the CO (3-0) overtone band in a high-purity CO sample of natural isotopic abundance were measured in five independent laboratories using different experimental techniques: Fourier transform spectroscopy (FTS) in DLR and PTB, cavity ring-down spectroscopy (CRDS) in NIM and NIST, and cavity mode-dispersion spectroscopy (CMDS) in NCU [1]. A set of 10 lines, measured by each of the laboratories, was chosen so that the ratio of the highest and the lowest line intensity was 240:1. In the case of each technique, some of the lines were beyond the optimal intensity range, as the sensitivity of FTS is typically significantly lower than in case of cavity-based techniques such as CRDS and CMDS. The line intensities were determined and compared with the results of the *ab initio* calculations given in Ref. [2].

A comparison of line intensities determined by different laboratories shows agreement at promille and subpromille levels. Weighted mean experimental values, having relative standard uncertainties of less than 1‰, show agreement with theory at 0.5‰ level. The presented approach shows that combined uncertainties in weighted-mean line intensities (including both statistical and systematic effects) can be reduced by coordinated experiments using multiple primary linear techniques that involve several independent laboratories.

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Pressure and temperature dependencies of air-perturbed O_2 *B*-band line shapes

***K. Bielska*[1] *, D. D. Tran*[1] *, A. A. Balashov*[1] *, J. Domysławska*[1] *, S. Wójtewicz*[1] *, M. Bober*[1] *, S. Bilicki*[1] *, R. Ciuryło*[1] *, D. Lisak*[1]**

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

Spectra of the air-broadened molecular oxygen B-band lines were measured with a high signal-to-noise ratio using frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) referenced to the optical frequency comb. Spectra measured at pressures below 200 Torr and temperatures between 288 K and 328 K were analyzed with the line-shape model considering the quadratic speed-dependence of collisional broadening and shift and the effect of velocity-changing collisions treated as hard collisions. The speed dependence and temperature dependence of collisional broadening and shift are determined. In addition, we have demonstrated that a reasonable estimation of temperature dependence for pressure broadening is possible even from spectra measured in a single temperature where the speed dependence of pressure broadening was determined. We have also improved line intensities, which were corrected by up to 3% compared to previously available data.

Our new spectroscopic data [1] improve the accuracy of the air-broadened oxygen B-band spectra description by order of magnitude. New line-shape parameters and intensities for 20 lines led to a 5-fold improvement in the B-band-based determination of the atmospheric vertical column density, reducing the difference between retrievals using *A*- and *B*-band lines [2].

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Ab initio quantum scattering calculations for N_2-perturbed $R(0)$ 3–0 line in CO

A. Olejnik[1] **, H. Jóźwiak**[1] **, N. Stolarczyk**[1] **, M. Żółtowski**[1] **, P. Wcisło**[1] **,**
H. Cybulski[2] **, B. Fernández**[3] **, C. Henriksen**[4]

[1] Inistitute of Physiscs, Faculty of Physics, Astronomy and Inormatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland, [2] Faculty of Physics, Kazimierz Wielki University, al. Powstancow Wielkopolskich 2, 85-090 Bydgoszcz, Poland, [3] Department of Physical Chemistry, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain, [4] Department of Applied Mathematics and Computer Science, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Carbon monoxide (CO) is a significant trace gas in Earth's atmosphere, contributing to climate change [1]. Its presence serves as an indicator of human activities, notably fossil fuel combustion [2]. Accurate measurements and theoretical predictions of CO's spectrum perturbed by N_2 and O_2 are vital for interpreting atmospheric absorption data [3].

We report the results of the first fully quantum scattering calculations for the N_2-perturbed R(0) 3-0 line in CO molecules, extending investigation for the pure rotational case [3]. Here we use a new five-dimensional potential energy surface. The calculations are performed using BIGOS, a new computational package developed in our group [4, 5]. The obtained scattering matrices (S-matrices) are used to provide the spectroscopic cross sections, which determine line broadening, shift and Dicke effect due to collisions [6]. In pararell, we carried out accurate CRDS line-shape measurements of this transition at three different temperatures. Our experimental data show good agreement with the theoretical results.

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N_2-collisional broadening of N_2O lines: high-resolution dual-comb spectroscopy and semi-classical line shape calculations

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Nitrous oxide is a strong greenhouse gas naturally present in the Earth's atmosphere, but also due to human activities. It plays an important role in the atmospheric chemistry and have a global warming potential 300 time higher than carbon dioxide. To monitor its concentration, accurate spectroscopic parameters are needed to accurately retrieve atmospheric spectra.

In this work, a high-resolution mid-infrared dual-comb spectrometer based on quantum cascade lasers (IRis-F1) [1] was used to determine collisional line shape parameters of N_2O lines diluted in N_2. The spectra were recorded at room temperature in the 1300 cm^{-1} spectral region. The line shape parameters were determined by adjusting the Voigt and speed-dependent Voigt models on the experimental line profiles using a multi-spectrum fitting technique. The obtained N_2-collisional broadening coefficients are in good agreement with literature.

Calculations with the Modified Complex Robert-Bonamy formalism [2] were made for the N_2O-N_2 molecular system using an intermolecular potential composed of electrostatic, atom-atom component expanded to the 20th order and rank 4, London dispersion and induction terms. The short-range interaction parameters were determined by reproducing the collisional half-width measured with IRis-F1 and available literature data for the same spectral region. Once the intermolecular potential is known, calculations for many other vibrational bands will be performed.

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Collisional excitation of PO^+ by *para*-H_2

F. Tonolo[1] **,** ***L. Bizzocchi***[1] **,** ***M. Melosso***[1] **,** ***C. Puzzarini***[1] **,** ***V. M. Rivilla***[2] **,**
F. Lique[3]

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When looking to the astrophysical networks that could be linked to abiogenesis (*i.e.*, the formation of prebiotic species from abiotic systems), phosphorus chemistry deserves a special attention [1]. The recent discovery of PO^+ in the G+0.693-0.027 molecular cloud [2] has prompted a collisional investigation of this ion to support the modeling of current and future observations in the interstellar medium (ISM). Hence, the molecular cloud under study possesses a relatively low density of H_2 gas, making local thermodynamic equilibrium (LTE) conditions unrealistic. To meet the astrophysical requirements, the collision between PO^+ and *para*-H_2 was thus examined [3]. The interaction potential energy surface (PES) was accurately characterized by computing a grid of energy points in the in the four Jacobi coordinates using the CCSD(T)-F12/aug-cc-pV(Q+d)Z level of theory, and the potential was then fitted as an expansion over angular functions. A comparison between *para*-H_2 and *ortho*-H_2 indicated a good agreement, suggesting that the results obtained with *para*-H_2 adequately describe the collisional behavior of PO^+. State-to-state collisional coefficients were then derived for the twenty lowest rotational levels of PO^+ at temperatures ranging from 5 to 200 K. These newly obtained collisional data allowed for testing the validity of the LTE approximation and helped to refine the H_2 density and column density estimation of PO^+ based on the observations of the G+0.693-0.027 molecular cloud. Additionally, radiative transfer calculations indicated a strong maser behavior for the first rotational transitions of PO^+ at various kinetic temperatures and densities typically found in interstellar sources. This emphasizes the importance of accurate collisional coefficients for precise modeling of the abundance of PO^+ in the ISM.

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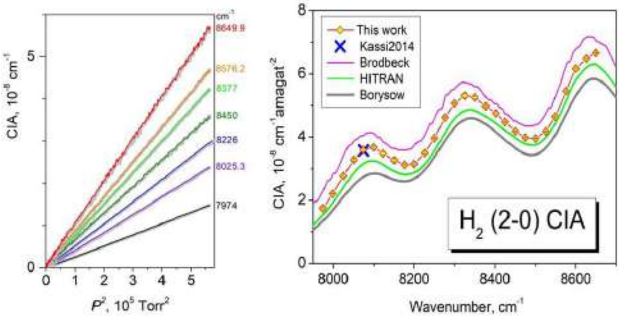
The collision-induced absorption of H_2 near 1.20 μm: subatmospheric measurements and validation tests of calculations

A. O. Koroleva[1] , ***S. Kassi***[1] , ***H. Fleurbaey***[1] , ***A. Campargue***[1]

[1] Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble (France)

The weak binary collision-induced absorption (CIA) of molecular hydrogen is measured at room temperature in the first overtone region near 1.20 μm [1]. Binary absorption coefficients are derived by cavity ring down spectroscopy (CRDS) at 28 selected spectral points sampling the (2-0) band between 7974 and 8650 cm^{-1}. While all previous studies used high density samples, the sensitivity of the CRDS method allowed deriving accurate CIA by using pressure ramps of pure H_2 limited to a maximum pressure of 1 atm (see Figure., left-hand). After subtraction of the Rayleigh contribution, a purely quadratic pressure dependence is obtained for the absorption coefficient at each measurement point and the CIA binary coefficients are derived with a 1.5% accuracy. The comparison to theoretical values widely used for astronomical applications shows deviations values between 5 and 25% (see Figure., right-hand).



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Contributed speaker FD1

Friday 6 September, 11:00
Chair: S. Alessandrini
Room D
Comparing theory and experiment

A full-symmetry torsion rotation theoretical approach for nitromethane CH_3NO_2

I. Gulaczyk[1] **, *M. Kreglewski***[1]

[1] Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poland

Nitromethane, CH_3NO_2, as a slightly asymmetric oblate rotor with a very low barrier to internal rotation, is a model molecule for studying the impact of free internal rotation on rovibrational spectroscopy. Because of its large-amplitude internal rotation, CH_3NO_2 is treated with the G_{12} molecular symmetry group, which is isomorphic to C_{6v} point group. The only allowed states of symmetry for nitromethane are A_1, A_2, E_2.

A new theoretical approach/program will be presented for nitromethane, which takes into account all symmetry properties of the molecule. A new approach for automatic labeling of torsion-rotation levels has been developed. The test was performed on previously assigned torsion-rotation spectra. The code will be also applied to the rotational spectrum recorded at the Swiss Light Source facility in the range 26-100 cm^{-1}.

Sweetness and light: computation of the rotational spectra of proto-saccharides

***M. Sang*[1] *, T. E. Field-Theodore*[1,2] *, P. R. Taylor*[1]**

[1]School of Pharmaceutical Science and Technology, Tianjin University, Tianjin, (PRC),
[2]Dipartimento di Chimica "Giacomo Ciamician", Universitá di Bologna, Bologna, (Italy)

To date, four $C_2H_4O_2$ isomers have been identified in the interstellar medium: methyl formate, glycolaldehyde, acetic acid, and (Z)-1,2-ethenediol [1, 2]. The detection of these species raises the question of whether other related carbohydrates could be present in similar astrophysical environments. In this study [3], we report a systematic investigation of six $C_2H_4O_2$ isomers not previously observed spectroscopically in space: anti-(1)-, (2)- and (3)-CH_2=CHOOH, methyldioxirane (c-(OOC)HCH_3), and anti- and syn-(2S)-oxiran-2-ol (cyc-C_2H_3-O)-OH). For each species, we employ coupled-cluster theory at the AE-CCSD(T)/cc-pCVQZ level to provide accurate equilibrium parameters, rotational constants, quartic centrifugal distortion parameters, and permanent electric dipole moment components. Anharmonic force fields were determined within vibrational perturbation theory to second order and evaluated using the MP2 method, thus allowing the evaluation of vibrational corrections. These computations provided, as a by-product, sextic centrifugal distortion constants. Rotational spectra have subsequently been simulated in the millimeter/submillimeter-wave frequency for the first time. It is hoped and anticipated that the accurate theoretical rovibrational spectral data presented herein will aid in experimental investigations of these title molecules in the interstellar medium.

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Millimeter-wave spectrum of 2-hydroxyacetophenone and 2-aminoacetophenone

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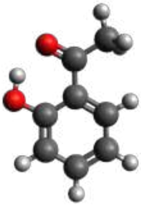
The rotational spectrum of 2-hydroxyacetophenone (2HAP) has been recorded and assigned using a Stark modulated Free-Jet Absorption Millimeter-Wave (FJ-AMMW) spectrometer in the 59.6-75.0 GHz frequency range. The results have been compared with quantum-mechanical data obtained at both the B3LYP-GD3(BJ)/Def2-TZVP) and MP2/aug-cc-pVTZ levels of calculation using the Gaussian16® software package. Only one conformer has been detected where a strong hydrogen bond between the acetyl oxygen atom and the hydroxyl atom takes place. The transition lines show a hyperfine structure due to internal rotation of the methyl group, which allowed the determination of a V_3=7.08(5) kJ mol^{-1} barrier. The structure of the observed conformer is similar to that of 2-aminoacetophenone (2AAP), which has been already investigated in the 2-8 GHz frequency range [1]. In this range the nuclear hyperfine structure due to the ^{14}N nuclear quadrupole coupling has been observed while no methyl internal rotation splitting was detected. New measurements with the FJ-AMMW spectrometer in a higher frequency region has allowed to observe some internal rotation splittings and determine V_3=8.22(8) kJ mol^{-1}, while no hyperfine structure due to the ^{14}N nuclear quadrupole coupling has been observed.


2HAP


2AAP

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Theoretical study of the CH_3Br+N_2 van der Waals complex: potential energy surface and applications

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The first five-dimensional potential energy surface (PES) for the CH_3Br + N_2 atmospheric weak bond complex is presented in this work. This surface is developed from a large number of ab initio energies where the CH_3Br (X^1A_1) and N_2 ($^1\Sigma^{+g}$) monomers are treated as rigid rotors. Computations were done using the DCSD/aug-cc-p-VTZ level of theory.For Br atom, we used the corresponding aug-ccpVTZ-PP correlation consistent basis set together with the appropriate Stuttgart/Köln ECP10MDF pseudopotential, where the ($3s^23p^64s^23d^{10}4p^5$) electrons are processed explicitly while the [Ne] electrons are part of the core. The equilibrium structure of the CH_3Br-N_2 complex found when N_2 is lying near the plane formed by the C_3 axis and the C–H bond at the inter-molecular separation of $7.58a_0$. The corresponding well depth is -300.97 cm^{-1}.

As a first application, this new 5D-PES is used for computing the temperature dependence of second virial coefficients of the CH_3Br + N_2 pair. Experimental values for a dimer CH_3Br gas mixture are not available to our knowledge. However, the data reported here will hopefully motivate this type of experiments, and will also serve as a future test of the quality of our surface.

As a second application, this PES is fitted to an analytical function through a procedure that combines spline, least-squares and projections for later evaluation of the pressure broadening coefficients of the spectral lines of Methyl bromide CH_3Br in N_2 bath. These data will be helpful to a precise estimation of CH_3Br abundances in planetary atmosphere spectra.

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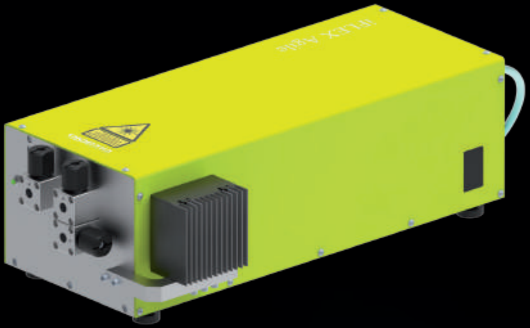
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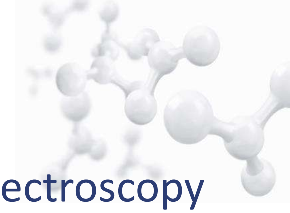

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	Sunday **01/09/24**	**Monday** **02/09/24**	**Tuesday** **03/09/24**	**Wednesday** **04/09/24**	**Thursday** **05/09/24**	**Friday** **06/09/24**
8:45 – 9:00	Arrival	Opening				Student prizes
9:00 – 10:30		MA plenary	Sessions TB1/TC1/TD1	WA plenary	ThA plenary	FA plenary
10:30 – 11:00		Break	Break	Break	Break	Break
11:00 – 12:30		Sessions MB1/MC1/MD1	Sessions TB2/TC2/TD2	Sessions WB1/WC1/WD1	Poster 2	Sessions FB1/FC1/FD1
12:30 – 14:00		Lunch	Lunch	Lunch‡	Lunch	Lunch
14:00 – 16:00		Sessions MB2/MC2/MD2	TA plenary	Free afternoon	Sessions ThB1/ThC1/ThD1	Departure
16:00 – 16:30	Registration Get together†	Break	Break*		Break	
16:30 – 18:30		Sessions MB3/MC3/MD3	Poster 1**		Free time Excursion	
18:30 – 22:30				Concert Social dinner		

† Get together until 19:30; * coffee break at 15:30; ** from 16:00 to 17:30; ‡ lunch at 13:00.