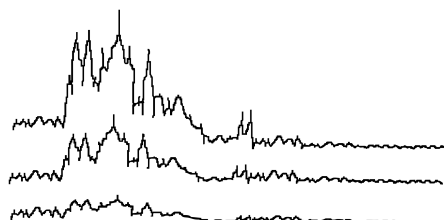


The 28th International Conference on High Resolution Molecular
Spectroscopy

*University of Chemistry and Technology, Prague, August 31 –
September 4, 2026*



Edited by:

Patrik Kania, Jan Koucký, Lucie Kolesníková, Kateřina Luková, Karel Vávra,
František Horák, and Štěpán Urban

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The 28th International Conference on High Resolution Molecular Spectroscopy

PRAHA2026

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University of Chemistry and Technology, Prague (UCT)

Technická 5, 166 28 Praha 6, Czechia

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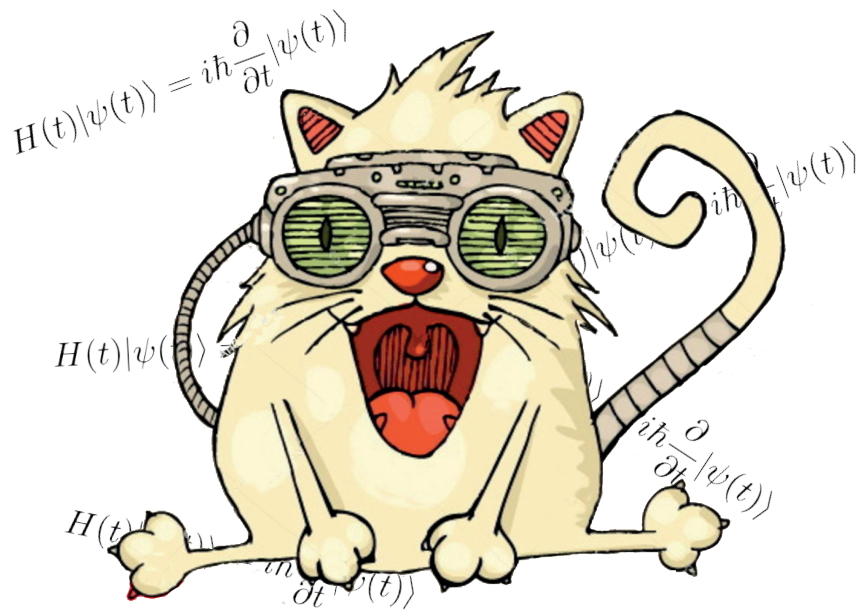
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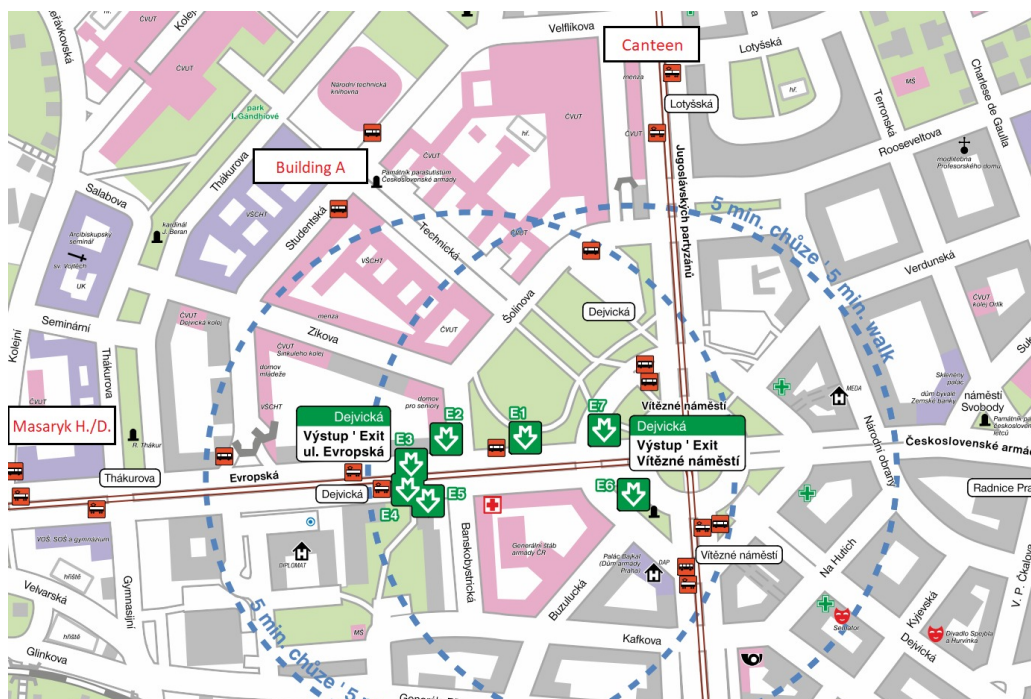
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	Sunday 30. 08. 2026	Monday 31. 08. 2026	Tuesday 01. 09. 2026	Wednesday 02. 09. 2026	Thursday 03. 09. 2026	Friday 04. 09. 2026
8:50–9:00		Welcome				
9:00–10:30		A Invited lectures K. MIZUSE J.-L. KUO AII	E Invited lectures S. BRÜNKEN J. CERNICCHARO AII	I Invited lectures Y. TAN L. RUTKOWSKI AII	L Invited lectures T. GIESEN W. J. BUMA AII	N Invited lectures B. BRODERICK S. YURCHENKO AII
10:30–11:00		Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
11:00–12:30		B (Exo)planetary Atmospheres AII	F Contributed talks AI/AII/B11	J Molecular Ion Spectroscopy AII	M Chirality & Chiral Recognition AII	O Contributed talks AI/AII
12:30–14:00		Lunch	Lunch	Lunch	Lunch	Lunch
14:00–16:00		C Contributed talks AI/AII/B11	G Contributed talks AI/AII/B11	Free afternoon	Free afternoon	
16:00–16:30		Coffee break	Coffee break			
16:30–18:00	Registration (16:00–22:00)	D Posters	H Posters	K IMIMS R. GENZEL	Concert (19:30–22:00)	
				Reception (18:30–22:00)		

IMIMS (9th Ioannes Marcus Marci Session): The Prague City Hall Auditorium; **Reception:** Residence of the Lord Mayor of Prague; **Concert:** Aula Magna, Carolinum

MAP AND DIRECTIONS



The Conference is held at the campus of the University of Chemistry and Technology Prague (UCT), located in Prague 6, Dejvice. The closest metro station is Dejvická (line A, green), and there is also a tram and a bus stop of the same name.

The UCT Prague campus in Dejvice consists of three buildings (A, B, and C). The conference takes place in building A, which was constructed between 1925 and 1933 according to the design of Prof. Antonín Engel. The main entrance to building A is located on Technická street.

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Program of Sessions

A: Invited Speakers

Monday, August 31, 2026, 09:00 – 10:30

Chair: Alberto Lesarri

- A1** – *MOLECULAR MOVIE SPECTROSCOPY OF WEAKLY-BOUND MOLECULAR CLUSTERS* (09:00 – 09:45)
Kenta Mizuse
- A2** – *APPLICATION OF AB INITIO ANHARMONIC ALGORITHMS TO UNDERSTAND QUANTUM RESONANCE IN VIBRATIONAL SPECTRA OF HYDRATES* (09:45 – 10:30)
Jer-Lai Kuo, Qian-Rui Huang

B: Mini Symposium: (Exo)planetary Atmospheres

Monday, August 31, 2026, 11:00 – 12:30

Chair: Vincent Boudon

- B1** – *(EXO)PLANETARY ATMOSPHERES* (11:00 – 11:30)
J. V. Seidel
- B2** – *INVESTIGATING THE ROVIBRATIONAL SPECTRUM OF HOPO* (11:30 – 11:45)
Ryan Mok, Oleksiy A. Smola, Sergey N. Yurchenko, Jonathan Tennyson
- B3** – *MACHINE LEARNING FOR ISOTOPOLOGUE EXTRAPOLATION IN THE EXOMOL PROJECT* (11:45 – 12:00)
Marco G. Barnfield, Jonathan Tennyson, and Sergey N. Yurchenko
- B4** – *TEMPERATURE DEPENDENT PHOTODISSOCIATION CROSS-SECTIONS AND RATES FOR MOLECULES OF ASTROPHYSICAL INTEREST* (12:00 – 12:15)
Ryan P. Brady, Andrei Sokolov, Charles Bowesman, Sergey N. Yurchenko, Jonathan Tennyson
- B5** – *HOLLOW CATHODE SLIT JET DISCHARGE SOURCE FOR SPECTROSCOPIC STUDIES OF METAL OXIDES AND HYDRIDES.* (12:15 – 12:30)
Ondrej Votava

C: Contributed Talks

Monday, August 31, 2026, 14:00 – 16:00

C-I (AI)

Chair: Jens-Uwe Grabow

- C-I.1** – *TRACKING THE STEPWISE HYDRATION OF THE TRIFLUOROACETIC ACID DIMER WITH ROTATIONAL SPECTROSCOPY* (14:00 – 14:15)
Megan A. Crutchfield, Farha S. Hussain, Nouredin Osseiran, Caroline S. Glick, George C. Shields, Alberto Lesarri, Amanda L. Steber, and Cristóbal Pérez
- C-I.2** – *WHEN WATER MEET CRESOL: A ROTATIONAL SPECTROSCOPIC STUDY OF CRESOL ISOMERS AND THEIR MICROSOLVATION* (14:15 – 14:30)
Agathe Maillard, Jordan A. Claus, Elias Neeman, S. Indira Murugachandran, Valerie Tsoi, Safia Hussain, Shefali Baweja, M. Eugenia Sanz, Noé Gallifa-Guynot, Isabelle Kleiner, Manuel Goubet
- C-I.3** – *ALIPHATIC VERSUS AROMATIC: IODINE-CONTAINING HALOGEN-BONDED COMPLEXES CHARACTERIZED BY HIGH-RESOLUTION MICROWAVE SPECTROSCOPY* (14:30 – 14:45)
Jannes N. Hasselhorn, Beppo Hartwig, Daniel A. Obenchain

- C-I.4** – *ENHANCING THE SIGMA-HOLE: HALOGEN BONDING IN PENTAFLUOROIODOBENZENE-WATER STUDIED BY ROTATIONAL SPECTROSCOPY* (14:45 – 15:00)
Andrea Maggio, Yue Liang, Assimo Maris, Weixing Li, Luca Evangelisti, Sonia Melandri
- C-I.5** – *FROM HYDROGEN BONDING TO DISPERSION FORCES: MOLECULAR COMPLEXES OF OXAZOLE WITH H₂O, NE AND CO₂ INVESTIGATED BY ROTATIONAL SPECTROSCOPY* (15:00 – 15:15)
J.R.Moran, C.Cabezas, D.Heras, S.De la Fuente, A.Lesarri, I.Peña
- C-I.6** – *IT TAKES TWO TO TANGO: HETEROATOM EFFECTS ON THE DIMERIZATION OF BENZOXAZOLE ISOMERS PROBED BY CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY* (15:15 – 15:30)
Freya E. L. Berggötz, Lisa Radtke, Melanie Schnell
- C-I.7** – *QUANTUM TUNNELING DYNAMICS OF WATER ON A PYRENE SURFACE* (15:30 – 15:45)
Nuno M. Campos, Rita J. C. Roque, Megan A. Crutchfield, Nouredin Osseiran, Farha S. Hussain, Amanda L. Steber, Cristóbal Pérez, Sérgio R. Domingos
- C-I.8** – *MICROSOLVATION OF WATER BY CO₂: THE STUDY OF WATER--(CO₂)_n BY QUANTUM CHEMISTRY AND ROTATIONAL SPECTROSCOPY, WITH UP TO n = 5* (15:45 – 16:00)
S. Collignon, A. J. Barclay, J. A. Claus, B. M. Hays, A. Pietropolli Charmet, A. R. W. McKellar, N. Moazzen-Ahmadi, C. Lauzin

C-II (AII)

Chair: Brooks H. Pate

- C-II.1** – *SEQUENTIAL CAVITY-MODE AUTO-LOCK SPECTROSCOPY (SCALS) OVER HUNDRED-TERAHERTZ RANGE WITH KILOHERTZ PRECISION* (14:00 – 14:15)
S. Vasilchenko, C.-X. Zuo, Y.-Q. Cheng, Z.-T. Zhang, W.-T. Wang, Y. R. Sun, Y. Tan, A.-W. Liu, S.-M. Hu
- C-II.2** – *HIGH-EFFICIENCY LASER SPECTROSCOPY ON COLD RADIOACTIVE MOLECULES USING CONTOURED NOZZLES* (14:15 – 14:30)
A. Claessens, R. Ferrer, Harshithbabu, W. Saelens, L. M. Arndt, Ch. E. Düllmann, F. Ivandikov, C. Murray, G. Neyens, J. Stricker, D. Renisch, P. Van den Bergh, P. Van Duppen, S. Wilkins
- C-II.3** – *HIGH-PRECISION SPECTROSCOPY OF H₂¹⁶O: IMPROVING THE SPECTROSCOPIC NETWORK THROUGH LAMB DIP AND TWO PHOTON ABSORPTION NICOHMS MEASUREMENTS* (14:30 – 14:45)
A. Altman, F.M.J. Cozijn, A. Bogomolov, R. Tóbiás, A.G. Császár, and W. Ubachs
- C-II.4** – *SINGLE-PHOTON DOPPLER-FREE SPECTROSCOPY IN THE VACUUM AND EXTREME ULTRAVIOLET* (14:45 – 15:00)
M. H. Rayment, B. Rub Schlie, J. A. Agner, H. Schmutz, F. Merkt
- C-II.5** – *TOWARDS HIGH RESOLUTION SPECTROSCOPY IN THE FAR-INFRARED RESTSTRAHLEN GAP USING NONLINEAR METASURFACE FOR DIFFERENCE FREQUENCY GENERATION* (15:00 – 15:15)
A. Zarin, J. Krakofsky, N.A. Chishti, J-F Lampin, M-H Mammez, M. Rieder, M-A Martin-Drumel, M. Belkin, O. Pirali
- C-II.6** – *ABSORPTION SPECTROSCOPY MEETS THE ACCURACY OF PURELY FREQUENCY-BASED DISPERSION SPECTROSCOPY* (15:15 – 15:30)
Rajesh Chell, Marcin Gibas, Daniel Lisak, Agata Cygan

C-II.7 – *PHASE-COHERENT CP-FT THZ EMISSION SPECTROSCOPY WITH A NBN HOT ELECTRON BOLOMETER* (15:30 – 15:45)

Roman A. Motiyenko, Eugen A. Alekseev, Sara Cibella, Guido Torrioli, Giacomo Gorla

C-II.8 – *MASER REFERENCED DISPLACEMENT SENSOR* (15:45 – 16:00)

C. Bragard, A. Altman, A. Bogomolov, A. Goodwin-Jones and C. Lauzin

C-III (B11)

Chair: Jer-Lai Kuo

C-III.1 – *WMS-ROT: FROM QUANTUM-CHEMICAL CALCULATIONS TO ASSIGNMENT-READY ROTATIONAL SPECTRA* (14:00 – 14:15)

Federico Lazzari

C-III.2 – *MACHINE-LEARNING CALIBRATION OF ROVIBRATIONAL ENERGY LEVELS OF CO₂ ISOTOPOLOGUES* (14:15 – 14:30)

M. T. I. Ibrahim, D. Alatoom, N. El-Kork, S. N. Yurchenko, J. Tennyson

C-III.3 – *ACETAMIDE: A STRANGE BREW OF STRUCTURE, SPECTROSCOPY AND THEORY* (14:30 – 14:45)

Terri E. Field-Theodore, Nicolò Quaresima, and Peter R. Taylor

C-III.4 – *NEW 4TH ORDER PARAMETER DEFINITIONS AND BRUTE FORCE APPROACH TO THE CONTACT TRANSFORMATION FOR THE G₆ TORSION-ROTATION PROBLEM* (14:45 – 15:00)

J.H. Westerfield, Helgi Rafn Hrodmarsson, Eléonore Antonelli, Mike Buttkus-Barth, Ha Vinh Lam Nguyen

C-III.5 – *HIGH-TEMPERATURE RAMAN SPECTRA OF CO₂ ISOTOPOLOGUES: MODELING WITH AN INTERACTING ANHARMONIC OSCILLATOR APPROACH* (15:00 – 15:15)

Eduardo Suárez, Christian Ostertag-Henning, Miguel Carvajal, Renato Lemus

C-III.6 – *AB INITIO COLLISION-INDUCED LINE SHAPE PARAMETERS FOR AIR-PERTURBED R(0) 0-0 LINE IN HF* (15:15 – 15:30)

Maksim Rachko, Jakub Behrendt, Hubert Józwiak, Artur Olejnik, Richard Dawes, Ernesto Quintas Sánchez, and Piotr Wcisło

C-III.7 – *RECENT ADVANCES IN HIGH-RESOLUTION SPECTROSCOPY OF ASTROPHYSICALLY IMPORTANT DIATOMIC MOLECULES* (15:30 – 15:45)

N. El-Kork, S. N. Yurchenko, J. Tennyson, and collaborators

C-III.8 – *VIBRATIONAL-ROTATIONAL SPECTROSCOPIC CHARACTERIZATION OF THE INTERSTELLAR COMPLEX ORGANIC MOLECULE METHYL ACETATE* (15:45 – 16:00)

Rossella Di Giovanni, Andrea Pietropolli Charmet, Paolo Stoppa, Nicola Tasinato

D: Posters

Monday, August 31, 2026, 16:30 – 18:00

D1 – *FUNDAMENTAL INVARIANT NEURAL NETWORKS APPLIED TO THE SPECTROSCOPY OF PROTONATED ACETYLENE*

L. H. Coudert

D2 – *THE ELECTRON SPIN-ROTATION-TORSION HAMILTONIAN ACCOUNTING FOR DISTORTION EFFECTS*

L. H. Coudert, R. Chahbazian, O. Pirali, M.-A. Martin-Drumel, L. Margulès, R. A. Motiyenko, and L. Zou

- D3** – *PRECISION SPECTROSCOPY FOR MEDICINE: PERSPECTIVES OF INTEGRATING BREATH-RELEVANT MOLECULES INTO HITRAN*
Frances M. Gomez, Robert J. Hargreaves, Iouli E. Gordon
- D4** – *EXPLORING THE CHIRALITY OF FLEXIBLE MOLECULES USING ROTATIONAL SPECTROSCOPY*
Wenhao Sun, Melanie Schnell
- D5** – *GROUND-STATE ENERGY LEVELS OF METHANE WITH kHz-LEVEL ACCURACY FROM COMB-REFERENCED DOUBLE-RESONANCE AND LAMB-DIP SPECTROSCOPIES*
Vinicius Silva de Oliveira, Isak Silander, Hiroyuki Sasada, Sho Okubo, Hajime Inaba, Kevin K. Lehmann, Aleksandra Foltynowicz
- D6** – *OPTICAL FREQUENCY COMB FOURIER TRANSFORM SPECTROSCOPY OF DIBROMOMETHANE IN THE 8 μ m REGION*
Ibrahim Sadiq, Aleksandr A. Balashov, Adrian Hjältén, Michael Rey, Oleg Egorov, Aleksandra Foltynowicz
- D7** – *TENTATIVE DETECTION OF SD^+ IN THE ORION BAR*
Mitsunori Araki, Valerio Lattanzi, Christian P. Endres, and Paola Caselli
- D8** – *BRIDGING THE METROLOGICAL GAP BETWEEN SPECTROSCOPIC LINE PARAMETERS AND SPECIES CONCENTRATIONS RETRIEVED BY GAS ANALYZERS.*
Victor Gorshelev, Gourab Dutta-Banik, Andrea Pogany, Jarvis Nwaboh
- D9** – *JET-COOLED ROTATIONAL SPECTROSCOPY OF ETHYL LACTATE: CONFORMATIONAL LANDSCAPES AND CONVERSIONS*
R. Hamidi Mejlej, A. Insausti, J. Ma, W. Jäger, and Y. Xu
- D10** – *GENERAL FITTING CODE: MAIN FEATURES AND APPLICATIONS*
Karel Vávra, Kateřina Luková
- D11** – *LABORATORY MILLIMETER- AND SUBMILLIMETER-WAVE SPECTROSCOPY OF THIOACETONE, FROM 150 TO 500 GHz FOR HOT-CORE SEARCHES*
Noé Gallifa-Guynot, Miguel Sanz-Novo, Víctor M. Rivilla, J.-C. Guillemin, Roman Motiyenko, and Laurent Margulès
- D12** – *QUANTUM CHEMISTRY CALCULATIONS OF EXCITED STATES OF CHIRAL DIMERS : A FIRST STEP TOWARDS TIME-RESOLVED CHIRAL RECOGNITION*
Clément Guiot du Doignon, José Luis Pascual, Ismanuel Rabadán, Bernard Pons
- D13** – *STEPWISE HYDRATION SWITCHES ELECTRONIC STRUCTURE IN A BIFUNCTIONAL ORGANOCATALYST THROUGH DOUBLE HYDROGEN BONDING*
Xiaolong Yi, Yongtao Wang, Haoran Li
- D14** – *HIGH-ACCURACY SPECTROSCOPY OF THE OXYGEN B BAND FOR ATMOSPHERIC REMOTE SENSING AND HITRAN2024*
K. Bielska, S. Wójtewicz, J. Domysławska, R. Ciuryło, D. Lisak
- D15** – *HIGH-ACCURACY HD LINE-SHAPE ANALYSIS WITH HETERODYNE CAVITY RING-DOWN SPECTROSCOPY*
Agata Cygan, Rajesh Chell, Szymon Wójtewicz, Hubert Józwiak, Grzegorz Kowzan, Nikodem Stolarczyk, Katarzyna Bielska, Piotr Wcisło, Roman Ciuryło, Daniel Lisak
- D16** – *SUB-DOPPLER SPECTROSCOPY OF METHANE IN THE THz RANGE*
Andela Zarin, Luan Juppert, Naveed Ahmed Chishty, Olivier Pirali
- D17** – *FIRST SPECTROSCOPIC STUDY OF A NEW INTERSTELLAR TARGET: ACETADIMINE ($HN=C(Me)NH_2$)*
Laurent Margulès, Noé Gallifa-Guynot, Roman A. Motiyenko, Jean-Claude Guillemin
- D18** – *RECENT DEVELOPMENTS OF THE LILLE ICE TERAHERTZ EXPERIMENT: IMPROVED SENSITIVITY AND APPLICATIONS TO PROCESSED ASTROPHYSICAL ICES*
Mariia Aliekseieva, Roman A. Motiyenko, Emmanuel Dartois

- D19** – *OBSERVATION AND DEPERTURBATION OF HIGHLY EXCITED STATES IS RBCS. EVIDENCE OF NON-ADIABATIC COUPLING*
W. Jastrzebski, J. Szczepkowski, A. Pashov, P. Kowalczyk
- D20** – *ROTATIONAL SPECTROSCOPIC STUDIES OF AN ODOROUS CHIRAL TAUTOMERIC FURANONE: 4-HYDROXY-2,5-DIMETHYL-3(2H)-FURANONE AND ITS HYDRATES*
Jiayi Li, Wenhao Sun, Liuting Wang, Melanie Schnell
- D21** – *CASDA24: CALCULATED DATABASES FOR MOLECULAR SPECTROSCOPY*
V. Boudon, C. Richard, O. Ben Fathallah, P. Hardy, R. Kamel, M. Rotger
- D22** – *TOWARDS UNDERSTANDING LEAK-OUT SPECTROSCOPY (LOS) IN CRYOGENIC ION TRAPS*
J. Böing, P. Schlemmer, E. Plaar, A. Sich, S. Schlemmer
- D23** – *NEW EXPERIMENTAL SPECTRA AND QUANTITATIVE MODELING OF THE STRETCHING DYAD OF SILANE AND OVERTONES*
Raef Kamel, Vincent Boudon, Cyril Richard, Fridolin Kwabia Tchana, and Laurent Bruel
- D24** – *RO-VIBRATIONAL SPECTROSCOPY OF THE ALLENE CATION ($C_3H_4^+$)*
Wenqin Li, Samuel J. P. Marlton, Meng Li, and Stephan Schlemmer
- D25** – *HIGH-RESOLUTION LEAK OUT SPECTROSCOPY OF THE ETHYLENE CATION*
Meng Li, Samuel J. P. Marlton, Wenqin Li, Stephan Schlemmer
- D26** – *HYPERFINE-RESOLVED VARIATIONAL NUCLEAR MOTION SPECTRA OF DI-ATOMIC MOLECULES*
Yide Yin, Sergey N. Yurchenko, and Jonathan Tennyson
- D27** – *THE ROTATIONAL SPECTRUM OF TRANS-2,3-EPOXYBUTANE: A COMBINED CHIRPED-PULSE FOURIER TRANSFORM AND ABSORPTION MICROWAVE STUDY*
Chenxu Wang, Rosemonde Chahbazian, Prachi Misra, Holger S. P. Müller, and Stephan Schlemmer
- D28** – *EXOMOL LINE LIST FOR LOW-LYING ELECTRONIC BAND SYSTEMS OF $^{12}C^{16}O$*
Chenyi Tao, Jonathan Tennyson, Sergei N. Yurchenko and Nayla El-Kork
- D29** – *REANALYSIS OF THE $B^2\Sigma^+ - X^2\Sigma^+$ SYSTEM OF $^{12}C^{17}O^+$ BY FT - UV EMISSION SPECTROSCOPY: $B^2\Sigma^+(\nu = 0, 1)$ LEVEL*
K. Jachymek, W. Szajna, R. Hakalla, S. Ryzner, A. Stasik, I. Piotrowska, M. I. Malicka, R. W. Field
- D30** – *EXTENSION OF 2-ETHOXYETHANOL ROTATIONAL SPECTROSCOPY AND ITS SEARCH IN ISM*
Agathe Maillard, D. Archie Stewart, Manuel Goubet, Elias M. Neeman, Brett A. McGuire
- D31** – *MODERN DFT SCALING FOR NUCLEAR QUADRUPOLE COUPLING CONSTANTS: QMBENCH.NET/NQCC/PARAMETRIZATION*
Jannes N. Hasselhorn, Beppo Hartwig, Daniel A. Obenchain
- D32** – *HIGH RESOLUTION SPECTROSCOPY OF EXOPLANET BIOSIGNATURES WITH LARGE AMPLITUDE MOTIONS*
T. K. L. Do, T. R. Huet, P. Asselin, Y. Berger, A. Rizopoulos, J. Vander Auwera, A. Maillard, M. Goubet, L. Zou, A. Cuisset, A. Roucou, R. George, A. Voute, H. V. L. Nguyen, and I. Kleiner
- D33** – *THE $^{13}C^{18}O$ $A^1\Pi(v = 2) \sim A^3\Pi(v = 13)$ INDIRECT PERTURBATION: DETECTION, MECHANISM AND SURPRISES*
S. Ryzner, R. W. Field, W. Ubachs, A. Pashov, P. Jasik, J. E. Sienkiewicz, N. de Oliveira, K. F. Lai, M. I. Malicka, A. Stasik, K. Jachymek, P. Kolek, R. Kępa W. Szajna, I. Piotrowska, A. Para, A. N. Heays, and R. Hakalla
- D34** – *HIGH-RESOLUTION SPECTROSCOPY OF $HCOOCH_3$, SKELETAL TORSION*
Ryoma Kakuda, Kaori Kobayashi, Masaharu Fujitake, Dennis W. Tokaryk, Brant E. Billinghurst

- D35** – *VACUUM COMPATIBLE PIEZO-ACTUATED MIRROR MOUNT WITH 80 KHZ BAND-WIDTH*
C. Bragard, A. Libert, A. Lorvelec, A. Bogomolov, A. Goodwin-Jones, and C. Lauzin
- D36** – *STUDY OF PREDISSOCIATIVE LIFETIMES OF CS^{2+} DICATION*
Lukáš Hrubčík, Tereza Uhlíková
- D37** – *CROSS-ISOTOPOLOGUE VALIDATION OF A RESIDUAL LIGHTGBM MODEL FOR CO_2 ENERGY CALIBRATION*
Mohammad Taha I. Ibrahim, Dunia Alatoom, Nayla El-Kork, Sergey N. Yurchenko, Jonathan Tennyson

E: Invited Speakers

Tuesday, September 01, 2026, 09:00 – 10:30

Chair: Oskar Asvany

- E1** – *BROADBAND VIBRATIONAL SPECTROSCOPY OF MOLECULAR IONS: FROM ASTROCHEMICAL FINGERPRINTS TO REACTION MECHANISMS* (09:00 – 09:45)
Sandra Brünken
- E2** – *THE SPACE AS A SPECTROSCOPIC LABORATORY: A NEW VIEW OF THE CHEMICAL COMPLEXITY IN THE UNIVERSE WITH THE QUIJOTE LINE SURVEY* (09:45 – 10:30)
José Cernicharo

F: Contributed Talks

Tuesday, September 01, 2026, 11:00 – 12:30

F-I (AI)

Chair: Marie-Aline Martin-Drumel

- F-I.1** – *DISSECTING INFRARED SIGNATURES IN INTERSTELLAR ICES BY INTEGRATED MATRIX-ISOLATION SPECTROSCOPY AND ANHARMONIC CALCULATIONS* (11:00 – 11:15)
Malgorzata Biczysko, Justyna Krupa
- F-I.2** – *HIGH-POWER LASER-PLASMA CHEMISTRY OF METHANOL VAPOR AND ITS DEUTERATED ISOTOPOLOGUES: SPECTROSCOPIC APPROACH* (11:15 – 11:30)
Veronika Horká-Zelenková, Josef Krása, Martina Toufarova, Jakub Cikhardt, Vojtěch Scheinpflug, Pooja Devi, Shubham Agarwal, Norbert Kanaloš, Roman Dudžák, Tomáš Burian, Michal Krupka, Sushil Singh, Libor Juha
- F-I.3** – *ANALYSIS OF THE HIGH RESOLUTION INFRARED SPECTRUM OF MONODEUTERO-OXIRANE IN THE $700\text{--}1000\text{ CM}^{-1}$ REGION* (11:30 – 11:45)
Karen Keppler, Alexandra Brandenberger, Michele Perrino, Jürgen Stohner, Ziqiu Chen, Sieghard Albert, Gunther Wichmann, Martin Quack
- F-I.4** – *VIBRATIONAL STARK EFFECT FOR PROBING LOCAL ELECTRIC FIELDS USING LASER SPECTROSCOPY* (11:45 – 12:00)
Fernando Torres-Hernández, Satchin Soorkia, Michel Broquier, Gilles Grégoire, Eric Gloaguen
- F-I.5** – *OPTICAL FREQUENCY COMB FOURIER TRANSFORM SPECTROSCOPY IN THE $8\text{ }\mu\text{m}$ REGION AND EFFECTIVE HAMILTONIAN LINE LIST OF FORMALDEHYDE* (12:00 – 12:15)
Aleksandr A. Balashov, Michael Rey, Adrian Hjältén, Aleksandra Foltynowicz

F-I.6 – *DUAL-FREQUENCY-COMB SPECTROSCOPY FROM THE TERAHERTZ TO THE VACUUM ULTRAVIOLET* (12:15 – 12:30)

Konstantin Vodopyanov, Dmitrii Konnov, Andrey Muraviev

F-II (AII)

Chair: Isabelle Kleiner

F-II.1 – *ROTATIONAL SPECTROSCOPY OF C-DEUTERATED AMINOACETONITRILE AND REFINEMENT OF ITS SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURE* (11:00 – 11:15)

Michela Nonne, Mattia Melosso, Luca Bizzocchi, Gabriele Panizzi, Silvia Alessandrini, Cristina Puzzarini

F-II.2 – *CONFORMATIONS OF THE MACROCYCLIC LACTONE HABANOLIDE: INFLUENCE OF THE DOUBLE BOND REVEALED BY ROTATIONAL SPECTROSCOPY* (11:15 – 11:30)

Charlotte N. Cummings, Gulnoor Anwar, and M. Eugenia Sanz

F-II.3 – *LARGE AMPLITUDE MOTIONS REVEALED BY FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY IN A POTENT ALKYLATING AGENT: METHYL METHANESULFONATE* (11:30 – 11:45)

Quentin Messaoudi, Sven Herbers, Beppo Hartwig, Kenneth Koziol, Ghita Oubouali, Guillaume Dhont, Ha Vinh Lam Nguyen, Luyao Zou

F-II.4 – *UNEXPECTEDLY LOW METHYL TORSIONAL BARRIERS IN THE MICROWAVE SPECTRUM OF 3-METHYL-2-THIOPHENECARBOXALDEHYDE RESOLVED AFTER A LONG-STANDING SPECTRAL ASSIGNMENT* (11:45 – 12:00)

M. Buttkus-Barth, C. Dindić, J. H. Westerfield, H. V. L. Nguyen

F-II.5 – *THREE METHYL INTERNAL ROTORS OF 3-ACETYL-2,5-DIMETHYLTHIOPHENE INVESTIGATED BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS* (12:00 – 12:15)

E. Antonelli, C. Dindic, H.V.L. Nguyen

F-II.6 – *SLIPPERY HANDSHAKES: MICROHYDRATION-DRIVEN EFFECTS IN ENANTIOSPECIFIC INTERACTIONS CAPTURED IN GAS-PHASE CLUSTERS* (12:15 – 12:30)

Rita J. C. Roque, Maria P. R. C. Marques, Nuno M. Campos, Sérgio R. Domingos

F-III (B11)

Chair: Wybren Jan Buma

F-III.1 – *PERTURBATION OF CO A¹Π BY a³Π SHOULD HAVE BEEN UNDETECTABLE: DETECTION, MECHANISM, AND SURPRISES* (11:00 – 11:15)

S. Ryzner, R. W. Field, W. Ubachs, A. N. Heays, A. Pashov, P. Jasik, J. E. Sienkiewicz, N. de Oliveira, K. F. Lai, M. I. Malicka, A. Stasik, W. Szajna, I. Piotrowska, and R. Hakalla

F-III.2 – *THE SPECTRUM OF CrD NEAR 800 nm RECORDED IN CAVITY-ENHANCED ABSORPTION* (11:15 – 11:30)

Jérôme Morville, Lucas K. A. Michaud--Chevalier, Amanda J. Ross

F-III.3 – *EXTENSIONS OF ASSIGNMENTS IN THE F⁴Δ-X⁴Δ SPECTRUM OF FeH: LOW-J LINES AND NEW VIBRATIONAL LEVELS* (11:30 – 11:45)

L. K. A. Michaud--Chevalier, T. E. Blackmore, D. W. Tokaryk, A. G. Adam, J. Morville, P. Crozet, A. J. Ross

- F-III.4** – *COMPETITION BETWEEN PHOTOIONIZATION AND PREDISSOCIATION IN ELECTRONICALLY EXCITED STATES OF He₂ STUDIED BY SIMULTANEOUS DETECTION OF METASTABLE He FRAGMENTS AND He₂⁺ IONS.* (11:45 – 12:00)
M. Holdener, J. Agner, H. Schmutz, F. Merkt
- F-III.5** – *DISENTANGLING FRANCK--CONDON AND HERZBERG--TELLER ACTIVITY IN THE S₁ ← S₀ SPECTRUM OF JET-COOLED STYRENE OXIDE: A COMBINED HIGH-RESOLUTION REMPI AND TDDFT STUDY* (12:00 – 12:15)
J. Jakob, M. Gerlach, V. Grigorian, P. Ferrari, T. F. Giesen, G. W. Fuchs
- F-III.6** – *FIRST ELECTRONIC SPECTRA OF VANADIUM HYDRIDE AND DEUTERIDE (VH/VD)* (12:15 – 12:30)
Thomas D. Varberg

G: Contributed Talks

Tuesday, September 01, 2026, 14:00 – 16:00

G-I (AI)

Chair: Sandra Brünken

- G-I.1** – *MILLIMETER-WAVE SPECTROSCOPY OF CORIOLIS-COUPLED MERCAPTOACETALDEHYDE (HCOCH₂SH)* (14:00 – 14:15)
Hayley A. Bunn, Brian J. Esselman, Zhenru Dong, Silvia Spezzano, Paola Caselli
- G-I.2** – *DETECTION OF S-BEARING SIX-MEMBERED RING IN THE LABORATORY AND IN SPACE* (14:15 – 14:30)
Mitsunori Araki, Miguel Sanz-Novio, Christian P. Endres, Paola Caselli, Víctor M. Rivilla, Izaskun Jiménez-Serra, Laura Colzi, Shaoshan Zeng, Andrés Megías, Álvaro López-Gallifa, Antonio Martínez-Henares, David San Andrés, Sergio Martín, Miguel A. Requena-Torres, Juan García de la Concepción, Valerio Lattanzi
- G-I.3** – *MILLIMETER-WAVE ROTATIONAL SPECTROSCOPY OF THIOPHENOL FOR ASTROCHEMISTRY* (14:30 – 14:45)
Zhenru Dong, Christian P. Endres, Mitsunori Araki, Paola Caselli, Valerio Lattanzi
- G-I.4** – *ROTATIONAL SPECTRUM AND STRUCTURAL ANALYSIS OF 5-NORBORNENE-2-CARBONITRILE: A BROADBAND MICROWAVE AND MILLIMETER-WAVE MICROWAVE STUDY* (14:45 – 15:00)
Domingo Heras, Carlos Cabezas, Isabel Peña, Celina Bermúdez, Alberto Lesarri
- G-I.5** – *ROTATIONAL SPECTROSCOPY OF CYANOCYCLOPENTADIENE ISOMERS AND DIAZOCYCLOPENTADIENE FOR ASTRONOMICAL SEARCH IN HOT INTERSTELLAR MEDIUM* (15:00 – 15:15)
Noé Gallifa-Guynot, Karina Sogomonyan, Brett A. McGuire, Jérôme Loreau, Roman Motiyenko, J.-C. Guillemin, and Laurent Margulès
- G-I.6** – *INVESTIGATING THE PRESENCE OF LARGER CYANO-DERIVATIVE PAHS IN THE INTERSTELLAR MEDIUM* (15:15 – 15:30)
Carlos Limeres Vazquez, Megan A. Crutchfield, Carlos Cabezas, Pablo Jurado, Farha S. Husain, José R. Morán, Isabel Peña, Alberto Lesarri, Celedonio M Alvarez, Dolores Pérez, José Cernicharo, Cristóbal Pérez, Amanda L. Steber
- G-I.7** – *FLASH VACUUM PYROLYSIS OF 1-METHYLCYCLOBUTANOL: INSIGHTS FROM ROTATIONAL SPECTROSCOPY* (15:30 – 15:45)
Lucie Kolesníková, Karel Vávra, Marie Kříž, Jan Svoboda, Patrik Kania, Štěpán Urban, Jean-Claude Guillemin

G-I.8 – *ROTATIONAL STUDY OF 1-AMINO-2-PROPANOL AND ITS VIBRATIONAL SATELLITES* (15:45 – 16:00)

P. Misra, M. Fatima, T. Gaßen, and S. Schlemmer

G-II (AII)

Chair: Sonia Melandri

G-II.1 – *CHAINING 4H-PYRAN-4-ONE: CONCERTED WATER DYNAMICS IN A PLANAR AROMATIC MOLECULE* (14:00 – 14:15)

Rita J.C. Roque, Nuno M. Campos, Donatella Loru, Eva Gougoula, Melanie Schnell, Sérgio R. Domingos

G-II.2 – *NON-LINEAR BIFURCATED HYDROGEN BONDS IN A PROTON SPONGE-FORMIC ACID COMPLEX REVEALED BY ROTATIONAL SPECTROSCOPY* (14:15 – 14:30)

Ningjing Jiang, Melanie Schnell

G-II.3 – *FROM TRIMER TO PENTAMER: STRUCTURAL MOTIFS AND INTERACTIONS IN SO₂ AGGREGATES* (14:30 – 14:45)

Satnam S. Dole, Chris Medcraft, S. Indira Murugachandran, M. Eugenia Sanz

G-II.4 – *REVEALING THE STRUCTURE AND INTERMOLECULAR INTERACTIONS OF 2-MERCAPTOETHANOL DIMERS BY BROADBAND ROTATIONAL SPECTROSCOPY* (14:45 – 15:00)

Farha S. Hussain, Nouredin Osseiran, Amanda L. Steber, and Cristóbal Pérez

G-II.5 – *UNVEILING THE UNDERAPPRECIATED: THE BONDING FEATURES OF C-H · · · S-S INTERACTIONS OBSERVED FROM ROTATIONAL SPECTROSCOPY* (15:00 – 15:15)

Wenqi Lv, Yugao Xu, Tingting Yang, Liuting Wang, Jinxi Huang, Haiying Huang, Gang Feng, Jens-Uwe Grabow

G-II.6 – *WATER- AND FORMIC ACID-ASSISTED CLAISEN REARRANGEMENTS PROBED BY ROTATIONAL SPECTROSCOPY* (15:15 – 15:30)

Xiujuan Wang, Jiayi Li, Melanie Schnell, Jens-Uwe Grabow

G-II.7 – *HIGH-RESOLUTION ROTATIONAL SPECTROSCOPY OF (OCS)_n--(H₂O)_m CLUSTERS* (15:30 – 15:45)

Z. Wang, D. Yélamos, C. Calabrese, C. Bermúdez, A. Lesarri

G-II.8 – *DISENTANGLING HYDROGEN VS. CHALCOGEN BONDING IN (HCl)₂ – H₂S AND HCl – H₂O – H₂S TRIMERS VIA BROADBAND ROTATIONAL SPECTROSCOPY* (15:45 – 16:00)

Megan A. Crutchfield, Nouredin Osseiran, Zbigniew Kisiel, Alberto Lesarri, Amanda L. Steber, Cristóbal Pérez

G-III (B11)

Chair: Dennis Tokaryk

G-III.1 – *SPECTROSCOPY OF MOLECULES, RADICALS, AGGREGATES BASED ON SILICON AND HYDROGEN* (14:00 – 14:15)

Raef Kamel, Vincent Boudon, Cyril Richard, Fridolin Kwabia Tchana, and Laurent Bruel

G-III.2 – *INFRARED SPECTROSCOPY OF ACETALDEHYDE IN SUPERFLUID HELIUM NANODROPLETS IN THE 3-MICRON REGION* (14:15 – 14:30)

R. Hamidi Mejlej, S. Parshotam, S.E. Beresnak, P. Raston, Q.R. Huang, J.L. Kuo, W. Jäger, and Y. Xu

- G-III.3** – *LINE INTENSITIES AND SELF-BROADENING COEFFICIENTS FOR THE ν_{14} BAND OF PYRROLE NEAR $14\ \mu\text{m}$ (14:30 – 14:45)*
Carla Silva Tafur, Jean Vander Auwera
- G-III.4** – *NEW SPECTROSCOPIC LINE PARAMETERS OF H_2O IN THE FAR-INFRARED REGION FOR ESA'S FORUM MISSION (14:45 – 15:00)*
Daniel Coxon, Jeremy Harrison, D. Chris Benner, Malathy Devi, Dominique Appadoo, Alexandre Voute, Brant Billingham, Jianbao Zhao, Alain Campargue
- G-III.5** – *INVESTIGATION OF DARK-STATE PERTURBATIONS IN THE ν_{17} METHYL ROCKING BAND OF PROPYLENE OXIDE BY THE $2\nu_{22} + \nu_{24}$ AND $\nu_{20} + \nu_{24}$ COMBINATION BANDS (15:00 – 15:15)*
B. Asadpour, T. F. Giesen, E. Döring, J. Jakob, K. Luková, K. Vávra, G. W. Fuchs
- G-III.6** – *SPECTROSCOPIC LINE PARAMETERS OF CARBON DIOXIDE IN THE $500\text{--}850\ \text{cm}^{-1}$ REGION (15:15 – 15:30)*
Jeremy J. Harrison, Daniel J.L. Coxon, D. Chris Benner, Malathy Devi, Brant E. Billingham, Jianbao Zhao
- G-III.7** – *INSIGHTS INTO THE $\text{HNCO} \cdots \text{H}_2\text{O}_2$ COMPLEXES BY MATRIX ISOLATION INFRARED SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS (15:30 – 15:45)*
L. Uribe, J. Krupa, M. Biczysko, and N. Tasinato
- G-III.8** – *HIGH RESOLUTION INFRARED, MICROWAVE AND MILLIMETER-WAVE SPECTROSCOPIES ON DIOXANE ISOMERS (15:45 – 16:00)*
Pierre Asselin, Alaa Houwayji, Manuel Goubet, Robert Georges, Anthony Roucou, Colwyn Bracquart, Olivier Pirali, Arnaud Cuisset

H: Posters

Tuesday, September 01, 2026, 16:30 – 18:00

- H1** – *TRIPLE-RESONANCE SPECTROSCOPY USING A FREQUENCY COMB PROBE FOR HIGH-PRECISION MEASUREMENTS OF METHANE IN THE $12,000\ \text{cm}^{-1}$ REGION*
Qinxue Nie, Vinicius Silva de Oliveira, Adrian Hjältén, Isak Silander, Kevin K. Lehmann, Aleksandra Foltynowicz
- H2** – *VUV-FT SPECTROSCOPY OF THE CAMERON SYSTEM ($\text{a}^3\Pi\text{--}\text{X}^1\Sigma^+$) AND DEPERTURBATION ANALYSIS OF THE $\text{a}^3\Pi$ ($\nu = 4$) STATE OF $^{12}\text{C}^{16}\text{O}$*
A. Stasik, R. W. Field, W. Ubachs, N. de Oliveira, S. Ryzner, M. I. Malicka, I. Piotrowska, K. Jachymek, A. Heays, W. Szajna, R. Hakalla
- H3** – *COLLISIONAL LINE BROADENINGS AND SHIFTS IN THE $S(0)$, $S(1)$ AND $S(2)$ ROTATIONAL RAMAN LINES OF HD IN AN H_2 BATH: EXPERIMENTAL MEASUREMENTS AND THEORETICAL CALCULATIONS*
R. Z. Martínez, L. Shirkov, H. Jóźwiak, P. Wcisło
- H4** – *ROVIBRATIONAL SPECTROSCOPY OF HNCO^+ : A POTENTIAL PRECURSOR OF HNCO IN SPACE*
Marius Gerlach, Samuel Marlton, Philipp Schmid, Jens van der Hulst, Sandra Brünken, Oskar Asvany, Stephan Schlemmer
- H5** – *AN IMPROVED STUDY OF CYANOACETYLENE AND DIACETYLENE INCLUDING THE STRONG $2\nu_5$ BAND OF HC_3N AND ν_4 BAND OF HC_4H*
Mattia Melosso, Luca Bizzocchi, Filippo Tamassia, Martina Taddia, Francesca Tonolo, Silvia Alessandrini, Gabriele Panizzi, Michela Nonne, Marie-Aline Martin-Drumel, Olivier Pirali, Luca Dore, Iouli E. Gordon, Cristina Puzzarini

- H6** – *GLOBAL ANALYSIS OF METHYL INTERNAL ROTATION AND EXACT NUCLEAR QUADRUPOLE COUPLING IN 2-CHLOROPROPENE*
E. Antonelli, J. Lhermenault, M.A. Pham, H.V.L. Nguyen
- H7** – *HIGH-RESOLUTION STUDY OF THE ν_{10} AND ν_9 BANDS OF ALLENE AROUND 11 μM*
Solène Perot, Athéna Rizopoulos, Jean Vander Auwera
- H8** – *HIGH-RESOLUTION SPECTROSCOPY AND MULTICHANNEL QUANTUM-DEFECT-THEORY ANALYSIS OF HIGH S AND D RYDBERG SERIES OF YTTERBIUM*
E. N. Toutoudaki, F. Merkt
- H9** – *INFRARED SIGNATURES OF REFRACTORY MOLECULES: FROM LABORATORY SPECTROSCOPY TO MIRA STARS*
Eileen Döring, Thomas F. Giesen, Guido W. Fuchs
- H10** – *FREQUENCY-MODULATED 200 GHz ROTATIONAL SPECTROSCOPY OF STYRENE OXIDE*
Caroline Maria Sunny, Jonas Bosmann, Guido W. Fuchs, Thomas F. Giesen
- H11** – *ROTATIONAL SPECTRA OF FOUR CONFORMERS OF ALLYLAMINE*
Kateřina Luková, Bao Ngoc Dangová, Lukáš Hrubčík, Tereza Uhlíková, Jan Koucký, Patrik Kania, Štěpán Urban, Lucie Kolesníková
- H12** – *TEMPERATURE-DEPENDENT PHOTODISSOCIATION CROSS SECTIONS AND RATES FOR NH AND H₂S*
Armando N. Perri, Tereza Uhlíková, Gap-Sue Kim, Alexander O. Mitrushchenkov, Sergey N. Yurchenko, and Jonathan Tennyson
- H13** – *ROVIBRATIONAL POPULATION REDISTRIBUTION IN JET-COOLED N₂O PROBED BY IR--MILLIMETER-WAVE DOUBLE RESONANCE*
J. Bosmann, T. F. Giesen, and G. W. Fuchs
- H14** – *OFF-AXIS CAVITY RING-DOWN SPECTROSCOPY OF JET-COOLED MOLECULES AT 3 μM*
Fabian Peterß, Xiaoyu Zhou, Thomas F. Giesen, Guido W. Fuchs
- H15** – *BENCHMARKING EDOT: PRECISE STRUCTURAL DETERMINATION OF THE MONOMER AND ITS WATER CLUSTER BY JET-COOLED ROTATIONAL SPECTROSCOPY*
Andrea Maggio, Jinxi Huang, Cristina Bagnacavalli, Luca Evangelisti, Assimo Maris, Sonia Melandri
- H16** – *COMPACT LASER ABLATION SOURCE SYSTEM FOR HIGH-RESOLUTION MOLECULAR SPECTROSCOPY*
Xiaoyu Zhou, Fabian Peterß, Thomas Giesen, Guido W. Fuchs
- H17** – *MICROWAVE SPECTRA OF 2-CHLORO-3-METHYLTHIOPHENE AND 2-CHLORO-5-METHYLTHIOPHENE: LOW-BARRIER METHYL INTERNAL ROTATION AND EXACT TREATMENT OF CHLORINE NUCLEAR QUADRUPOLE COUPLING*
K. J. Koziol, H. V. L. Nguyen
- H18** – *¹³C- AND ¹⁵N-MONOSUBSTITUTED ISOTOPOLOGUES OF HC₃N: CHARACTERIZATION OF THE RESONANCE SYSTEMS*
G. Panizzi, M. Nonne, L. Bizzocchi, M. Melosso, S. Alessandrini, and C. Puzzarini
- H19** – *COMPARATIVE ROTATIONAL SPECTROSCOPIC STUDY OF HYDRATED CO₂ AND SO₂ MOLECULAR CLUSTERS*
Z. Wang, D. Yélamos, E. Neeman, A. Lesarri, C. Bermúdez, C. Calabrese
- H20** – *THE HIGH RESOLUTION SPECTRUM OF THE ν_2 BAND OF THE ELUSIVE HSCO⁺*
José Luis Doménech, Wesley G. D. P. Silva, Valerio Lattanzi, Sven Thorwirth, Stephan Schlemmer, and Oskar Asvany

- H21** – *HIGH-RESOLUTION INFRARED SPECTROSCOPY OF N₂O BROADENED BY HE, AND H₂ TO ASSIST IN ANALYSIS OF EXOPLANETARY ATMOSPHERES.*
Himanshi Singh, Hayley A. Bunn, Silvia Spezzano, Laura Schöller, Paola Caselli
- H22** – *LASER SPECTROSCOPY OF FeH: CHARACTERIZING THE MAGNETIC RESPONSE OF SELECT LEVELS IN THE A⁴Π STATE*
T. E. Blackmore, D. W. Tokaryk, A. G. Adam, P. Crozet, A. J. Ross
- H23** – *MOLECULAR-LEVEL INSIGHTS INTO CO₂ CAPTURE AND COMPETITIVE BINDING WITH WATER IN ORTHO-FLUOROANILINE: A ROTATIONAL STUDY*
R. B. L. Vieira, A. Nunes, N. M. Campos, R. J. C. Roque, S. R. Domingos
- H24** – *AN AB INITIO ROVIBRATIONAL LINELIST FOR HPO*
Ryan Mok, Fangping Liu, Sergey N. Yurchenko
- H25** – *PROBING THE SURFACE CHEMISTRY TOWARDS INTERSTELLAR DUST GRAINS: (SUB-)MILLIMETER-WAVE SPECTROSCOPIC CHARACTERIZATION OF NH₂CL*
Michela Nonne, Audrey Coutens, Elias Neeman, Jean-Claude Guillemin, Manuel Goubet, Valérie Vallet, Olivier Pirali, Holger S. P. Müller, Jean-Christophe Loison, Marie-Aline Martin-Drumel
- H26** – *MACHINE LEARNING IN THE EXOMOL PROJECT*
Joseph S. Andrews, Marco G. Barnfield, Elizabeth R. Guest, Sergey N. Yurchenko, and Jonathan Tennyson
- H27** – *3,3,4,4,5,5,6,6,6-NONAFLUOROHEXAN-1-OL: A COMBINED ROTATIONAL SPECTROSCOPY AND QUANTUM-CHEMICAL STUDY OF A PARTIALLY FLUORINATED ALIPHATIC ALCOHOL*
Filippo Baroncelli, Tommaso Coccia, Andrea Vasquez, Aran Insausti, Luca Evangelisti, Assimo Maris, Emilio J. Cocinero, Sonia Melandri
- H28** – *INFRARED AND MICROWAVE SPECTROSCOPY OF (CO)₂ - WATER TRIMERS AND OBSERVATION OF A NEW SYMMETRIC ISOMER*
Simon Collignon, Aaron J. Barclay, Jordan A. Claus, Andrea Pietropoli Charmet, Andrew R. W. McKellar, Clément Lauzin, Nasser Moazzen-Ahmadi
- H29** – *BRIDGING THEORY AND EXPERIMENT: CO-N₂ 3-0 BAND CASE STUDY*
Klaudia Chętnik, Artur Olejnik, Nikodem Stolarczyk, Michał Żółtowski, Hubert J. Jóźwiak, Michał Słowiński, Szymon Wójtewicz, Katarzyna Bielska, Piotr Masłowski, Hubert Cybulski, Berta Fernández, Christian Henriksen, Agata Cygan, Roman Ciuryło, Daniel Lisak, Piotr Weisło
- H30** – *NEW BEYOND-VOIGT LINE-SHAPE PROFILE RECOMMENDED FOR THE HITRAN DATABASE*
Michał Słowiński, Piotr Weisło, Nikodem Stolarczyk, Hubert J. Jóźwiak, Daniel Lisak, Roman Ciuryło, Agata Cygan, Franz Schreier, Christopher D. Boone, Antonio Castrillo, Livio Gianfrani, Yan Tan, Shui-Ming Hu, Erin M. Adkins, Joseph T. Hodges, Ha Tran, Ngoc Hoa Ngo, Jean-Michel Hartmann, Serge Béguier, Alain Campargue, Robert J. Hargreaves, Laurence S. Rothman, Iouli E. Gordon
- H31** – *A COMPLETE ROVIBRATIONAL LEVEL SCHEME FOR NH₃ NEAR 7000 CM⁻¹*
Peter Čermák, Karvan Kaushal, Ondřej Votava
- H32** – *PRECISION COHERENT MICROWAVE SPECTROSCOPY OF THE R(0) TRANSITION OF OCS IN A KU-BAND WAVEGUIDE*
Simon Collignon, Dimitri Lederer, Clément Lauzin
- H33** – *ACCURATE ROVIBRONIC LINE LISTS OF HYDROGEN FLUORIDE*
Nariman Abu El Kher, Sergey N. Yurchenko, Nayla El-Kork
- H34** – *WIDE-RANGE FROST-POINT MEASUREMENT USING A CRDS-BASED MINIATURIZED SENSOR*
Hisashi Abe

- H35** – *EXPLORING HIGH AND LOW METHYL TORSIONAL BARRIERS IN 2-CHLOROPICOLINES: THE MICROWAVE SPECTRA OF 2-CHLORO-3-PICOLINE AND 2-CHLORO-PICOLINE*
M. Buttkus-Barth, H. V. L. Nguyen
- H36** – *TORSIONAL VIBRATIONS AND SYMMETRY OF $B(OH)_3$: TESTING THE UNITED CONFIGURATION APPROACH TO SELECTED NON-RIGID MOLECULES*
George Pitsevich, Alex Malevich
- H37** – *CAN DVR AND FOURIER METHODS REPRODUCE THE EXACT $(2\ell + 1)$ — FOLD DEGENERACY OF THE FREE RIGID ROTOR?*
George Pitsevich, Alex Malevich

I: Invited Speakers

Wednesday, September 02, 2026, 09:00 – 10:30

Chair: Konstantin Vodopyanov

- I1** – *OPTICAL FREQUENCY COMB SPECTROSCOPY IN COLD AND NON-EQUILIBRIUM MOLECULAR ENVIRONMENTS* (09:00 – 09:45)
Lucile Rutkowski
- I2** – *PRECISION COLLISIONAL LINE-SHAPE ANALYSIS AND QUANTUM GAS METROLOGY VIA ALL-FREQUENCY-DOMAIN SPECTROSCOPY* (09:45 – 10:30)
Yan Tan, Shui-Ming Hu, Jin Wang, Jin-Ke Li, Qi Huang, Hui Liang, Chang-Le Hu

J: Mini Symposium: Molecular Ion Spectroscopy

Wednesday, September 02, 2026, 11:00 – 12:30

Chair: José Luis Doménech

- J1** – *REVEALING HIGH-RESOLUTION SPECTRA OF HYDROCARBON CATIONS WITH LEAK-OUT SPECTROSCOPY* (11:00 – 11:30)
Oskar Asvany, Philipp Schmid, Wesley Silva, Divta Gupta, Samuel J. P. Marlton, Thomas Salomon, Sven Thorwirth and Stephan Schlemmer
- J2** – *DEUTERONATED FORMALDEHYDE IN FOCUS: THEORY AND EXPERIMENT* (11:30 – 11:45)
Denis Comte, Mattia Melosso, Hunarpreet Kaur, Dennis F. Dinu, Ernest A. Michael, Terri E. Field-Theodore, Wesley G. D. P. Silva, Silvia Alessandrini, Luca Bizzocchi, Sven Thorwirth, Klaus R. Liedl, Sandra Brünken, Cristina Puzzarini, Stephan Schlemmer, Oskar Asvany
- J3** – *HIGH RESOLUTION ROVIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF HC_3N^+* (11:45 – 12:00)
Eline Plaar, Annemarie Sich, Oskar Asvany, Sven Thorwirth, Wesley G. D. P. Silva and Stephan Schlemmer
- J4** – *HIGH-RESOLUTION SPECTROSCOPY OF ELUSIVE PROTONATED METHANOL ($CH_3OH_2^+$)* (12:00 – 12:15)
Wesley G. D. P. Silva, Oskar Asvany, Sven Thorwirth, Isabelle Kleiner, Iwona Gulaczyk, Marek Kreglewski, Miguel Sanz-Novo, Victor M. Rivilla, and Stephan Schlemmer
- J5** – *ELECTRONIC LEAK-OUT SPECTROSCOPY OF COLD ASTROPHYSICALLY RELEVANT IONS IN THE GAS PHASE AND SEARCH FOR DIBS.* (12:15 – 12:30)
Le Schneider, Samuel J. P. Marlton, Eline Plaar, Robin Jacobi

K: Ioannes Marcus Marci Session

Wednesday, September 02, 2026, 16:30 – 18:00

Chair: José Cernicharo

- K1** – *MASSIVE BLACK HOLES AND GALAXIES: EXPERIMENTAL EVIDENCE AND COSMIC CO-EVOLUTION* (16:30 – 17:15)
Reinhard Genzel

L: Invited Speakers

Thursday, September 03, 2026, 09:00 – 10:30

Chair: Cristóbal Pérez

- L1** – *PUTTING LIGHT TO CHEMICAL USE: FROM SPECTATOR TO ACTIVATOR* (09:00 – 09:45)
Wybren Jan Buma
- L2** – *CHIRAL MOLECULES ACROSS ROTATIONAL, VIBRATIONAL AND ELECTRONIC SCALES: FROM MOLECULAR FINGERPRINTS TO ENANTIOSELECTIVE DETECTION AND CONTROL* (09:45 – 10:30)
Thomas Giesen

M: Mini Symposium: Chirality and Chiral Recognition

Thursday, September 03, 2026, 11:00 – 12:30

Chair: Maria Eugenia Sanz and Melanie Schnell

- M1** – *TESTING MECHANISMS FOR ASYMMETRIC SYNTHESIS USING CHIRAL TAG ROTATIONAL SPECTROSCOPY* (11:00 – 11:30)
Brooks H. Pate
- M2** – *VIBRATIONAL SPECTROSCOPY AND PHOTOELECTRON CIRCULAR DICHROISM OF CHIRAL COMPLEXES* (11:30 – 12:00)
Anne Zehnacker
- M3** – *SPIN-CHIRALITY COUPLING WITHOUT MAGNETIC FIELDS* (12:00 – 12:15)
Philip Flores, Stefanos Carlström, Serguei Patchkovskii, Misha Ivanov, Andres Ordonez, Olga Smirnova
- M4** – *PROBING CHIRAL RECOGNITION IN THE CARVONE-1-PHENYLETHANOL COMPLEX BY ROTATIONAL SPECTROSCOPY* (12:15 – 12:30)
S. Indira Murugachandran, M. Eugenia Sanz

N: Invited Speakers

Friday, September 04, 2026, 09:00 – 10:30

Chair: Daniel Obenchain

- N1** – *CONNECTING INTERSTELLAR ICE CHEMISTRY TO ASTRONOMICAL OBSERVATIONS: LABORATORY CONSTRAINTS FOR MOLECULAR ASTROPHYSICS* (09:00 – 09:45)
Bernadette M. Broderick
- N2** – *ACROSS WAVELENGTHS AND TOWARDS HIGH RESOLUTION: EXOMOL FOR JWST, ARIEL AND THE ELT ERA* (09:45 – 10:30)
Sergey Yurchenko

O: Contributed Talks

Friday, September 04, 2026, 11:00 – 12:30

O-I (AI)

Chair: Amanda Ross

- O-I.1** – *STARK-SHIFT DOUBLE-RESONANCE SPECTROSCOPY OF EXCITED STATES IN HIGH POLYADS OF METHANE* (11:00 – 11:15)
 Vinicius Silva de Oliveira, Adrian Hjältén, Michael Rey, Yuan Cao, Andrea Rosina, Kevin K. Lehmann, Aleksandra Foltynowicz
- O-I.2** – *FREQUENCY COMB-CALIBRATED ROTATIONALLY RESOLVED SPECTRUM OF THE H₂O–CO₂ VAN DER WAALS COMPLEX IN THE 30H RANGE* (11:15 – 11:30)
 A.S. Bogomolov, S. Collignon, N. Moazzen-Ahmadi, M. Herman, and C. Lauzin
- O-I.3** – *OPTICAL GAS THERMOMETRY AND AMOUNT-OF-SUBSTANCE METROLOGY USING CAVITY MODE-DISPERSION SPECTROSCOPY* (11:30 – 11:45)
 D. Lisak, S. Wójtewicz, A. Cygan, P. Wcisło, R. Ciuryło, K. Bielska
- O-I.4** – *CAVITY-ENHANCED SPECTROSCOPY IN THE DEEP CRYOGENIC REGIME FOR QUANTUM SENSING AND METROLOGY* (11:45 – 12:00)
 Michał Słowiński, Kamil Stankiewicz, Marcin Makowski, Kamil Leon Sołtys, Bogdan Bednarski, Hubert Joachim Jóźwiak, Nikodem Stolarczyk, Mateusz Narożnik, Dariusz Kierski, Szymon Wójtewicz, Agata Cygan, Grzegorz Kowzan, Piotr Masłowski, Mariusz Piwiński, Daniel Lisak, Piotr Wcisło
- O-I.5** – *SUB-KHZ VIBRATIONAL FREQUENCY MEASUREMENTS VIA MID-INFRARED SATURATION ABSORPTION SPECTROSCOPY* (12:00 – 12:15)
 S. Viel, M.N. Ngo, Y. Liu, N. Cahuzac, M. Saffre, D.B.A. Tran, R. Santagata, T. Durier, B. Dutta, E. Cantin, O. Lopez, A. Amy-Klein, G. L. Ngo, L. Lucia, S. Pirotta, A. Bousseksou, R. Colombelli, M. Manceau, B. Darquié
- O-I.6** – *METROLOGY OF THE HELIUM DIMER WITH A SPECTRAL RESOLUTION OF 2.5 PPB AND A PRECISION OF 15 PPT* (12:15 – 12:30)
 Vincent Wirth, Janosch Jörg, Frédéric Merkt

O-II (AII)

Chair: Mattia Melosso

- O-II.1** – *FIRST LIGHT OF A NEW 5.5–18 GHz BROADBAND CRYOGENIC BUFFER GAS COOLING CP-FTMW SPECTROMETER* (11:00 – 11:15)
 Megan A. Crutchfield, Noureddin Osseiran, Lincoln Satterthwaite, Alberto Lesarri, Amanda L. Steber, and Cristóbal Pérez
- O-II.2** – *SIX-FOLD METHYL INTERNAL ROTATION AND ¹⁴N NUCLEAR QUADRUPOLE COUPLING IN THE MICROWAVE SPECTRA OF N-METHYLMALIMIDE AND N-METHYLSUCCINIMIDE* (11:15 – 11:30)
 Safa Khemissi, Chisom A. Tiu, Isabelle Kleiner, Ha Vinh Lam Nguyen, Kyle Crabtree, A. O. Hernandez-Castillo
- O-II.3** – *THIONATION TO THIOPIVALIC ACID: FROM SYNTHESIS TO A BROAD MICROWAVE ANALYSIS USING A VARIETY OF SPECTROSCOPIC TECHNIQUES* (11:30 – 11:45)
 K. J. Koziol, K. R. Leopold

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- O-II.4** – *MICROSOLVATION AND STRUCTURAL EVOLUTION OF METHYL ETHYL AND DIETHYL SULFOXIDES IN WATER CLUSTERS PROBED BY ROTATIONAL SPECTROSCOPY* (11:45 – 12:00)
Liuting Wang, Wenhao Sun, Melanie Schnell
- O-II.5** – *ROTATIONAL OBSERVATION OF OPEN-SHELL SINGLET PERSISTENT RADICAL PAIRS* (12:00 – 12:15)
Yongtao Wang, Wenqin Li, Xiaolong Yi, Xinyu Wang, Meng Li, Jens-Uwe Grabow, Carlos Cabezas, Ibon Alkorta, Cristóbal Pérez, Alberto Lesarri, Haoran Li
- O-II.6** – *NON-COVALENT INTERACTIONS OF PHTHALIDE HYDRATES STUDIED BY ROTATIONAL SPECTROSCOPY* (12:15 – 12:30)
V. Tsoi, J. A. Claus, E. Neeman, M. Goubet, and M. E. Sanz

A: Invited Speakers

Monday, August 31, 2026, 09:00

Chair : Alberto Lesarri

MOLECULAR MOVIE SPECTROSCOPY OF WEAKLY-BOUND MOLECULAR CLUSTERS

Kenta Mizuse^{1,2}

¹Kitasato University, Department of Chemistry

²Institute of Science Tokyo, Department of Chemistry

Molecular spectroscopy is often referred to as the “observation of molecular motions,” although conventional spectra provide only an indirect measure of dynamics. Recent advances in ultrashort laser techniques and imaging methods have overcome this limitation, enabling us to record “molecular movies” that capture real-time structural and orientational motions as vibrational and rotational wave packet dynamics. What kind of spectroscopic information can we extract from such movies? I will show that “movie-based spectroscopy” (wave packet imaging spectroscopy) successfully addresses this question, simultaneously offering broad bandwidth (>3 THz), high resolution (~ 50 MHz), and definitive spectral assignments directly derived from the recorded wave packet movies. This method combines an

impulsive Raman excitation using a broadband femtosecond pump pulse with a real-time probe via Coulomb explosion imaging. Fourier transformation of the observed time-trace movie yields high-resolution Raman spectra, while the movie itself visually reveals exact molecular motions at specific frequencies, providing intuitive insights to disentangle complex spectral features (Figure 1).

Studying weakly-bound molecular clusters is crucial for understanding intermolecular interactions; however, measuring and analyzing both pure rotational (microwave) and intermolecular vibrational (THz) spectra with a single experimental setup has long been a challenge. To demonstrate the high versatility of time-domain Raman spectroscopy and the unique effectiveness of movie-based spectroscopy, we applied this approach to various van der Waals systems, including Ar_2 , Kr_2 , $\text{N}_2\text{-Ar}$, $(\text{N}_2)_2$, $(\text{C}_2\text{H}_2)_{2,3}$, rotationally-resolved vibrational states of van der Waals clusters, and larger species such as π -stacked clusters. Details on the experimental setup, selected results, and future prospects of this method will be presented in this talk.

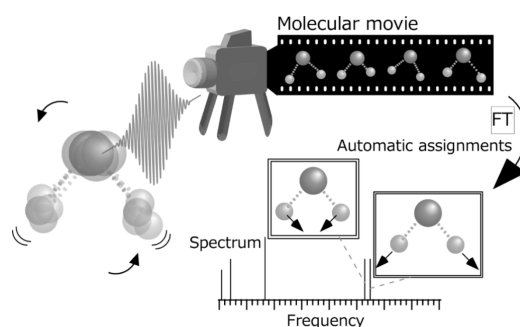


Figure 1: Figure 1. Concept of molecular movie spectroscopy

APPLICATION OF AB INITIO ANHARMONIC ALGORITHMS TO UNDERSTAND QUANTUM RESONANCE IN VIBRATIONAL SPECTRA OF HYDRATES

Jer-Lai Kuo¹, Qian-Rui Huang¹

¹Institute of Atomic and Molecular Sciences, Academia Sinica

The vibration spectra of OH stretch in water are known for different types of quantum resonance attributed to various anharmonic coupling (such as Fermi resonance and combination bands) to explain their complex vibrational features. Over the last twenty years, experimental IRPD spectra of $\text{H}_2\text{O} \cdots \text{X}^-$, where $\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{CN}, \text{NC}, \text{mNP}^{1,4}$, are found to exhibit complex but well resolved vibrational features between $2800\text{--}3400\text{ cm}^{-1}$ (as shown in Figure 1). While above-mentioned anharmonic coupling schemes have been proposed to explain some of these peculiar splitting of hydrogen-bonded OH stretch bands under different solvation conditions, there is a lack of a unifying picture. In this talk, we will present how we can use ab initio anharmonic algorithms (that is computational algorithms without using empirical parameters to fit to experimental data) to reveal the quantum resonance underneath the observed spectra and to track their originations to the anharmonic couplings among the different vibrational degrees of freedom of H_2O in these complexes.

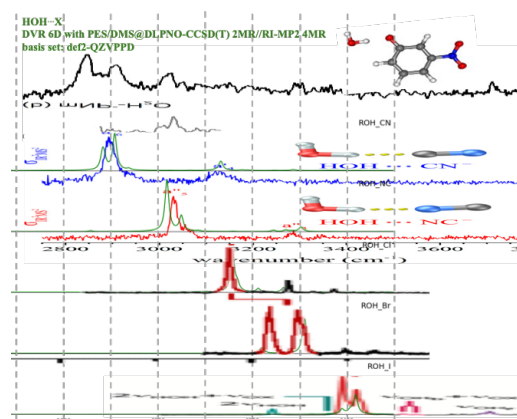


Figure 2: Experimental IRPD spectra of $\text{H}_2\text{O} \cdots \text{X}^-$, where $\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{CN}, \text{NC}, \text{mNP}^{[1-4]}$ and absorption spectra simulated with PES/DMS from DLPNO-CCSD/def2-QZVPPD (green).

1. J. R. Roscioli, E. G. Diken, M. A. Johnson, S. Horvath and A. B. McCoy, *J. Phys. Chem. A* 110, 4943 (2006)
2. S. Horvath and A. B. McCoy, B. Elliott, G. H. Weddle, J. R. Roscioli, and M. A. Johnson *J. Phys. Chem. A* 114, 1156 (2010)
3. J. T. Kelly, H. Knorke, Knut R. Asmis, *J. Phys. Chem. Lett.*, 8, 5349 (2017)
4. F. L. Molina, Q-R Huang, M. Broquier, S. Soorkia, G. A. Pino, J-L Kuo and Gilles Grégoire, *J. Phys. Chem. A*, 27, 20614 (2025)

**B: Mini Symposium: (Exo)planetary
Atmospheres**

Monday, August 31, 2026, 11:00

Chair : Vincent Boudon

(EXO)PLANETARY ATMOSPHERES

J. V. Seidel¹

¹Observatoire de la Côte d’Azur, Lagrange Laboratory, Nice, France

High-resolution spectroscopy has transformed our understanding of exoplanetary atmospheres. By resolving individual spectral lines, it allows us to identify atmospheric species, probe planetary climates and dynamics, and study worlds spanning an extraordinary range of physical and chemical conditions. As new facilities such as the Extremely Large Telescope (ELT) promise observations of unprecedented quality, one challenge is becoming increasingly apparent: our ability to interpret these data is only as good as the molecular line lists on which they rely.

In this talk, I will discuss why accurate molecular spectroscopy has become a key ingredient for exoplanet atmosphere studies and highlight several examples where incomplete or inaccurate line lists limit our ability to detect or characterize molecules. These challenges are particularly pressing in spectral regions such as the optical and UV and temperature regimes that are challenging to compute and even more difficult to measure in the laboratory.

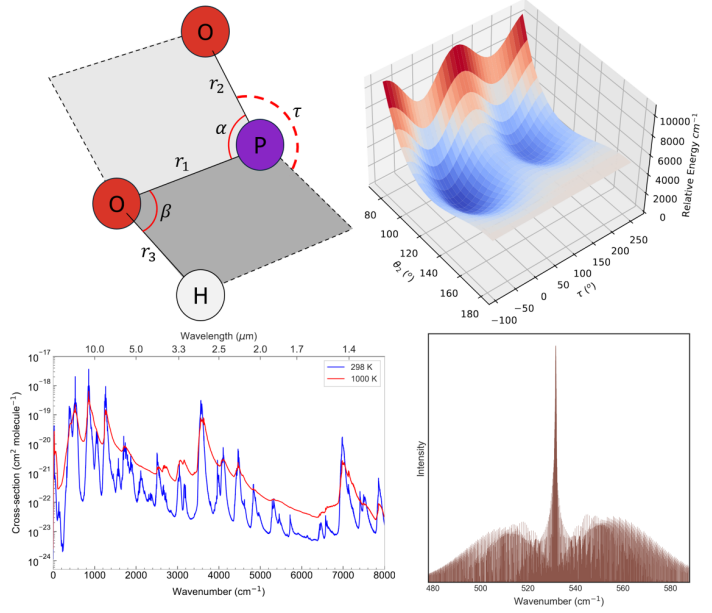
I will also argue that the relationship between these two fields is not one-sided. Planetary atmospheres provide access to physical conditions that are difficult—or impossible—to reproduce in the laboratory, making them powerful natural testbeds for molecular spectroscopy. By confronting theoretical and laboratory line lists with observations of increasingly diverse planetary atmospheres, we can leverage these natural laboratories to improve molecular lists.

INVESTIGATING THE ROVIBRATIONAL SPECTRUM OF HOPO

Ryan Mok¹, Oleksiy A. Smola¹, Sergey N. Yurchenko¹, Jonathan Tennyson¹

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

Photochemical models identify the tetratomic molecule HOPO as a dominant phosphorus carrier in metallicity enriched warm-Neptune and hot-Jupiter exoplanets - replacing PH_3 which is broken apart by photodissociation. While HOPO can be suggested as a target for astronomical detection, modeling its rovibrational spectrum is complicated by *cis-trans* isomerism and low tunneling barriers. Starting from *ab initio* calculation, new CCSD(T)-F12 potential energy and dipole moment surfaces are produced. We introduce novel implementations within the nuclear motion program TROVE to treat simultaneous tunneling between *cis* and *trans* conformations through torsion and bending modes. A key feature utilised is the new Summed Product Analytic Representation (SPAR) framework to generalise handling potential and dipole functions alongside the kinetic energy operator. As a result, we compute vibrational transitions within several wavenumbers of experiment, transition intensities and an absorption cross-section for states $J = 0$ to 40. This study establishes the first steps required for a HOPO linelist to model exoplanet atmospheres.



MACHINE LEARNING FOR ISOTOPOLOGUE EXTRAPOLATION IN THE EXOMOL PROJECT

Marco G. Barnfield, Jonathan Tennyson, and Sergey N. Yurchenko

¹Department of Physics and Astronomy, University College London

Since 2011, the ExoMol database has provided molecular line lists and energy levels underpinning the modelling of hot atmospheres, including those of exoplanets, brown dwarfs, and cool stars, and now hosts over 1 trillion transitions across 100+ molecules and 250+ isotopologues. The growing use of these line lists in High-Resolution Cross-Correlation Spectroscopy to detect molecular species in exoplanet atmospheres sharpens an existing accuracy challenge: parent isotopologues are typically well characterised, but minor isotopologues, essential for constraining planetary formation and evolutionary history via isotope ratios, often lack experimental validation and rely on less accurate theoretical predictions.

The isotopologue extrapolation (IE) method, introduced by Polyansky *et al.* [1], then formalized by McKemmish *et al.* [2], addresses this by modelling the residual error between calculated and empirical (MARVEL) energy levels of a data-rich parent isotopologue, then transferring this correction to isotopologues lacking experimental data. A fully-connected neural network implementing IE for CO₂ reduces the mean absolute error relative to the original method for over 87% of levels, and a hybrid transfer-learning architecture propagates these correction patterns to the data-poor CO system, improving 93% of samples and yielding updated line lists for 11 CO₂ isotopologues [3]. Work is now underway on a graph neural network (GNN) formulation of IE that represents an isotopologue network as a single connected graph, correcting all isotopologues jointly rather than one at a time.

A parallel effort applies GNNs to the empirical side of this pipeline: a shared-encoder, multi-task network trained on MARVEL transition networks predicts energy-level uncertainties, flags anomalous transitions, proposes links across orphaned sub-networks, and suggests quantum-number relabelling directly from network topology. Validated on published CO and CO₂ MARVEL datasets, its uncertainty predictions already exceed both the legacy MARVEL estimate and the published values, and its label-correction head recovers the correct assignment for over 88% of corrupted lines. Together, these two GNN-based approaches point towards a fully data-driven pipeline linking empirical network validation to theoretical isotopologue prediction, both central to improving the accuracy and completeness of the ExoMol database.

References:

- [1] O. L. Polyansky, A. A. Kyuberis, L. Lodi, J. Tennyson, R. I. Ovsyannikov, and N.F. Zobov. ExoMol molecular line lists XIX: high accuracy computed line lists for H₂¹⁷O and H₂¹⁸O. MNRAS, 466:1363–1371, 2017. doi: 10.1093/mnras/stw3125.
- [2] L. K. McKemmish, C. A. Bowesman, K. Kefala, A. N. Perri, A. M. Syme, S. N. Yurchenko, and J. Tennyson. A hybrid approach to generating diatomic line lists for high resolution studies of exoplanets and other hot astronomical objects: Updates to ExoMol MgO, VO and TiO line lists. RASTI, 3:565–583, 2024. doi: 10.1093/rasti/rzae037.
- [3] M. G. Barnfield, O. L. Polyansky, S. N. Yurchenko, and J. Tennyson. Machine learning isotope shifts in molecular energy levels. J. Mol. Spectrosc., 418-419:112084, 2026. doi: 10.1016/j.jms.2026.112084.

TEMPERATURE DEPENDENT PHOTODISSOCIATION CROSS-SECTIONS AND RATES FOR MOLECULES OF ASTROPHYSICAL INTEREST

Ryan P. Brady¹, Andrei Sokolov¹, Charles Bowesman¹, Sergey N. Yurchenko¹, Jonathan Tennyson¹

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

Within environments subject to UV-rich radiation fields, such as molecular clouds, stellar, and planetary atmospheres, photochemical processes have a strong influence on composition and dynamics. To date, major data repositories provide cross-sections and photodissociation rates for molecular temperatures of 0 K, where only the ground vibronic level is populated. While sufficient for describing cold objects like the interstellar medium, a new frontier in modern astrophysics has emerged. The modelling and interpretation of (exo)planetary spectra require the accurate description of molecular photochemistry, particularly the temperature dependence thereof, as lower-state thermal populations lead to significant changes in cross-sections and rates.

To address this, rigorous treatment of many excited electronic states and their respective couplings is not only required to yield accurate UV spectroscopy, but also for the determination of predissociation and photodissociation rates. Generating these spectra requires overcoming the theoretical challenges of these highly excited states; namely, the breakdown of the Born-Oppenheimer approximation. By incorporating rigorous diabatisation treatments into our variational rovibronic codes, we are able to successfully generate accurate molecular line lists and capture non-adiabatic-induced predissociation, alongside usual dissociation mechanisms (e.g., spin-orbit induced predissociation, direct photoabsorption).

Building on our successful application to several diatomic molecules, we present our recent work on computing temperature-dependent UV spectra and photodissociation cross-sections using sulfur monoxide (SO) and carbon monohydride (CH) as examples. We demonstrate our approach for calculating temperature-dependent photodissociation rates across various radiation fields. Our results reveal that a molecule's photodissociation rate is heavily dependent on its temperature. We highlight how the proper treatment of this temperature dependence is essential for breaking parameter degeneracies in current photochemical networks and accurately characterising high-temperature astrophysical environments.

HOLLOW CATHODE SLIT JET DISCHARGE SOURCE FOR SPECTROSCOPIC STUDIES OF METAL OXIDES AND HYDRIDES.

Ondrej Votava¹

¹Heyrovský Institute of the CAS, Dolešková 2155/3 Praha 8, Czech Republic

Wide range of metal oxides and metal hydrides have been detected in atmospheres of cold stars and are expected in the atmospheres of hot rocky exoplanets on short orbits. Their detection in exoplanetary atmospheres relies on techniques such as high-resolution cross-correlation spectroscopy (HRCCS) which requires reliable laboratory spectroscopic data. However, producing such species in the laboratory with sufficient abundances for spectroscopic studies represents a significant challenge. In this work-in-progress contribution I present recent development of laboratory source for in-situ synthesis of relevant molecular species such as AlO, CrO, NiH, and TiH in cold supersonic expansions. The source evolves from slit-jet discharge radical source originally introduced by Nesbitt and coworkers, yet employs hollow cathode geometry to enhance metal sputtering and subsequent reactions with oxygen and/or hydrogen gas in the sub-sonic region of the gas flow.

The source will be integrated into the Prague high resolution diode laser spectrometer with the goal to characterize the spectra of metal hydrides and metal oxides in the near-IR spectral range.

C-I: Contributed Talks

Monday, August 31, 2026, 14:00

Chair : Jens-Uwe Grabow

AI

TRACKING THE STEPWISE HYDRATION OF THE TRIFLUOROACETIC ACID DIMER WITH ROTATIONAL SPECTROSCOPY

Megan A. Crutchfield¹, Farha S. Hussain¹, Nouredin Osseiran³, Caroline S. Glick², George C. Shields², Alberto Lesarri¹, Amanda L. Steber¹, and Cristóbal Pérez^{3,4}

¹Departamento de Química Física y Química Inorgánica, Facultad de Ciencias-I.U.

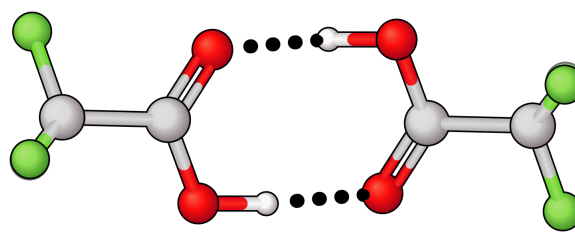
²Department of Chemistry, Furman University, Greenville, SC 29613, USA

³Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS)

⁴Oportunus. Axencia Galega de Innovación, 15702 Santiago de Compostela, Spain.

Rotational spectroscopy provides a powerful approach for probing the structures of molecular aggregates and the evolution of hydrogen-bonding networks during solvation. Hydrated molecular dimers represent ideal model systems for investigating the earliest stages of solvation, where the competition between intermolecular interactions and water-mediated hydrogen bonding dictates the resulting structures. In this work, broadband Chirped-Pulse Fourier Transform Microwave (CP-FTMW) spectroscopy, combined with high-level quantum chemical calculations, was used to investigate the stepwise hydration of

the trifluoroacetic acid (TFA) dimer. Rotational spectra of the TFA dimer and its hydrated complexes, $(\text{TFA})_2 \cdot \text{H}_2\text{O}$, $(\text{TFA})_2 \cdot (\text{H}_2\text{O})_2$, and $(\text{TFA})_2 \cdot (\text{H}_2\text{O})_3$, were recorded in the 2–18 GHz frequency range using a supersonic jet expansion. The assigned spectra reveal how the hydrogen-bonding network evolves with the sequential addition of water molecules. In particular, the experimentally observed dihydrate adopts a kinetically trapped structure rather than the predicted global minimum, demonstrating that cluster formation in the supersonic expansion is governed by kinetic effects as well as thermodynamic stability. These results provide molecular-level insight into the early stages of hydration of fluorinated carboxylic acids and highlight the sensitivity of rotational spectroscopy for characterizing subtle intermolecular interactions in isolated molecular clusters.



TFA₂

WHEN WATER MEET CRESOL: A ROTATIONAL SPECTROSCOPIC STUDY OF CRESOL ISOMERS AND THEIR MICROSOLVATION

Agathe Maillard¹, Jordan A. Claus², Elias Neeman¹, S. Indira Murugachandran³, Valerie Tsoi³, Safia Hussain³, Shefali Baweja³, M. Eugenia Sanz³, Noé Gallifa-Guynot¹, Laurent Margulès¹, Isabelle Kleiner⁴, Manuel Goubet¹

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

²Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgique

³Department of Chemistry, King's College London, London SE1 1DB, United Kingdom

⁴Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, F 75013 Paris, France

The study of organic compounds present in particulate matter such as Secondary Organic Aerosols (SOAs), resulting from gas-phase oxidation reactions of Volatile or semi-Volatile Organic Compounds (VOCs, SVOCs), is essential for understanding the chemical composition of our atmosphere. Cresols, substituted phenols produced during the photo-oxidation of toluene ¹, an abundant atmospheric pollutant, are of particular interest due to their environmental prevalence and toxicity to humans. Cresols are aromatic compounds featuring a methyl and an hydroxyl substituents on a benzene ring. The relative position of these groups lead to three structural isomers: *ortho*, *meta*, and *para*. The methyl rotor induces large-amplitude internal rotation that strongly couples with the overall molecular rotation. Consequently, the rotational spectra require treatment with dedicated torsion-rotation Hamiltonians, which considerably complicates the spectroscopic analysis.

Here, we focus on the characterisation of the *syn* and *anti* conformers of *ortho*-cresol and its microsolvation, as well as on the microsolvation of *para*-cresol. To this end, a combination of experimental and theoretical approaches was employed. Quantum chemical calculations were first made to explore the conformational landscape of the different conformers and water complexes, estimate their molecular parameters and predict their rotational spectrum. Rotational spectra in the (sub)millimetre-wave ranges were recorded to characterise *ortho*-cresol aiming to complete previous investigations in the centimetre range ². The microsolvated complexes of the *ortho* and *para* isomers were studied using both broadband and narrowband experiments in the centimetre range ³.

These results provide insight into the early stages of atmospheric cluster formation and the role of hydrogen bonding in SOA formation.

¹R. M. Zhang, D. G. Truhlar & X. Xu, "Kinetics of the toluene reaction with OH radical." Research, DOI: 10.34133/2019/5373785 (2019).

²A. Welzel, A. Hellweg, I. Merke & W. Stahl, "Structural and torsional properties of o-cresol and o-cresol-OD as obtained from microwave spectroscopy and ab initio calculations." J. Mol. Spectrosc., 215, 58, DOI: 10.1006/jmsp.2002.8600 (2002).

³The French State under the France-2030 program and the Initiative of Excellence of the Université de Lille are acknowledged for the funding and support granted under the R-CDP-24-003-AREA project.

ALIPHATIC VERSUS AROMATIC: IODINE-CONTAINING HALOGEN-BONDED COMPLEXES CHARACTERIZED BY HIGH-RESOLUTION MICROWAVE SPECTROSCOPY

Jannes N. Hasselhorn¹, Beppo Hartwig^{1,2}, Daniel A. Obenchain¹

¹Institute of Physical Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany

²Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, 94010, Créteil, France

Halogen atoms are typically associated with accumulated electron density. They act as hydrogen bond acceptors and form salts. Depending on the binding situation, however, they can exhibit an area of electron depletion, known as a σ -hole, which can be visualized as a positive electrostatic potential.[1] This phenomenon is particularly pronounced for heavy halogen atoms when they are bonded to electron-withdrawing substituents. This electrophilic area can form an attractive interaction with a nucleophilic area, known as a halogen bond. Halogen bonds have numerous applications, such as in crystal engineering.[1]

High-resolution rotational spectroscopy can provide a deeper, more fundamental understanding of this interaction in the gas phase. Consequently, halogen-bonded systems have been studied, the group of A. C. Legon has been instrumental in this research. While some systems have been characterized experimentally, such as CF₃I and ICl combined with H₂S and PH₃ (examples of donors and acceptors), these experiments were limited to relatively light, symmetric systems.[2]

Here, we present experimental results from cavity resonator Fourier transform microwave jet spectroscopy of the complex formed by the halogen bond donors heptafluoro-2-iodopropane and pentafluoroiodobenzene with the acceptor pyridine. The first is likely the heaviest halogen bond ever studied by rotational spectroscopy. The latter is the first halogen bonded complex of two aromatic monomers. We discuss and compare the experimental results against each other, to theory, and to systems studied previously, developing a possible correlation between the force constants that describe the stretching of the complex partners against each other and the gas-phase basicities. Additionally, we derive valence p-orbital occupations and ionic characters through a systematic implementation of Novick's extended Townes–Dailey model [3,4,5] to gauge the effects of aromaticity and hybridization.

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ENHANCING THE SIGMA-HOLE: HALOGEN BONDING IN PENTAFLUOROIODOBENZENE-WATER STUDIED BY ROTATIONAL SPECTROSCOPY

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Fluorine, with its strong electron-withdrawing properties, can drastically alter the electron distribution of a molecular scaffold compared to its unsubstituted counterpart. In fluorinated aromatic rings, fluorine substituents deplete the pi-system of electron density, generating a positive electrostatic potential region perpendicular to the ring plane, termed a pi-hole.

This perfluorination-induced electronic perturbation has a direct effect on the electron anisotropy of the halogen atom. While highly polarizable halogens (Cl, Br, I) inherently exhibit a sigma-hole¹ (a positive electrostatic potential along the C–X bond axis) and a nucleophilic equatorial belt,² the introduction of perfluorination drastically enhances this anisotropy, amplifying the magnitude of the sigma-hole and allowing the halogen atom to engage in highly directional non-covalent interactions known as halogen bonds.³

In this work, pentafluoroiodobenzene has been characterized by combining quantum chemical calculations and chirped-pulse rotational spectroscopy in the 2 - 8 GHz frequency range. The assignment of the ¹³C isotopologue spectra enabled a precise structural determination and the effect of perfluorination on the electron anisotropy of the iodine atom was quantified through the semiempirical extended Townes–Dailey (ETD)⁴ model and Natural Bond Orbital (NBO) calculations, demonstrating an enhancement of the sigma-hole⁵ when compared with the results for its hydrogenated counterpart, iodobenzene. This same effect is observed in chlorobenzene and bromobenzene, passing from the hydrogenated species to the perfluorinated analogues.⁶

The enhancement of the sigma-hole induced by perfluorination is further highlighted by the formation of non-covalent clusters. As a next step, the characterization of pentafluoroiodobenzene–water clusters was undertaken. Both quantum chemical calculations and experimental data indicate that the most stable structure is the one in which water binds to perfluoroiodobenzene via a halogen bond, with the water oxygen donating electron density to the positive sigma-hole on iodine, rather than through the more conventional hydrogen bond.

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FROM HYDROGEN BONDING TO DISPERSION FORCES: MOLECULAR COMPLEXES OF OXAZOLE WITH H₂O, NE AND CO₂ INVESTIGATED BY ROTATIONAL SPECTROSCOPY

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Non-covalent interactions (NCIs) play a crucial role in the formation, growth, stability, and reactivity of atmospheric clusters, aerosols, and trace-gas complexes. Although oxazole is not considered a major atmospheric constituent, it serves as a suitable model nitrogen-containing heterocyclic volatile organic compound (VOC) for investigating the interactions of heteroaromatic species with atmospherically relevant molecules. In this work, oxazole molecular complexes with H₂O, CO₂, and Ne were studied using a combination of broadband chirped-pulse Fourier transform microwave (CP-FTMW) rotational spectroscopy and quantum-chemical calculations. Six complexes including oxazole–H₂O, oxazole–(H₂O)₂, oxazole–CO₂, oxazole–(H₂O)(CO₂), oxazole–Ne, and oxazole–Ne₂ were identified in the 2-8 GHz frequency range, from which the spectroscopic constants and structural parameters were derived. The hydration complexes reveal the preferred hydrogen-bonding sites around the oxazole ring and the effects of sequential water addition. The oxazole–CO₂ and oxazole–(H₂O)(CO₂) complexes shed light on the interaction of heteroaromatic compounds with carbon dioxide, highlighting the balance between hydrogen-bonding and dispersion forces. These results provide a molecular-level framework for understanding the interactions underlying selective CO₂ recognition and separation. In contrast, the oxazole–Ne and oxazole–Ne₂ complexes offer benchmark systems for probing weak intermolecular interactions dominated by dispersion forces.

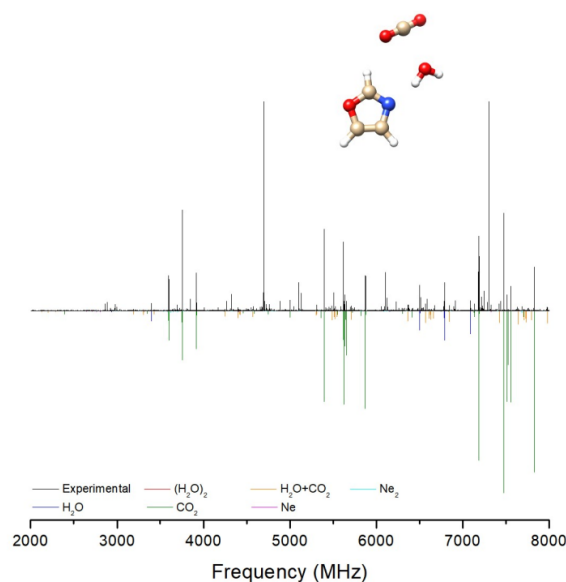


Figure 3: Broadband rotational spectra of the oxazole–CO₂ and oxazole–H₂O complexes recorded using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy.

IT TAKES TWO TO TANGO: HETEROATOM EFFECTS ON THE DIMERIZATION OF BENZOXAZOLE ISOMERS PROBED BY CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

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For the dimers of aromatic systems, two characteristic structural motifs have been identified: edge-to-face geometries that are dominated by CH- π interactions, as it has been found in the distorted T-shaped benzene dimer¹, and parallel-displaced orientations that are dominated by π - π dispersion interactions.² The aromatic bicyclic heterocycles anthranil, indoxazine, and benzoxazole (Figure 1) provide an ideal platform for systematically investigating how the introduction

and positional arrangement of the heteroatoms oxygen and nitrogen influence intermolecular interactions and dimer formation, as the three isomers differ only in the relative positions of the heteroatoms. The rotational spectrum of each molecular sample was measured in the 2–12 GHz frequency range using the chirped-pulse Fourier transform microwave spectrometer COMPACT. Supported by quantum chemical calculations, the spectra were assigned and rotational constants, centrifugal distortion constants, and nuclear quadrupole coupling constants were determined for one dimer of each isomer. Experiments and calculations show a clear preference for parallel-displaced geometries that are stabilized by π - π dispersion interactions. At the same time, the relative positions of the heteroatoms influence the degree of parallel alignment and the relative displacement of the monomers.

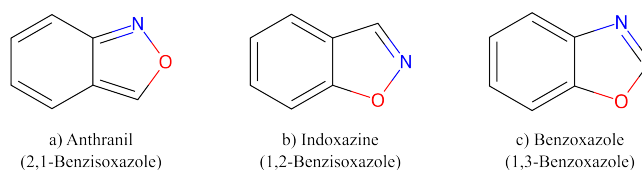


Figure 4: Skeletal formula of the three structural isomers anthranil, indoxazine, and benzoxazole.

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QUANTUM TUNNELING DYNAMICS OF WATER ON A PYRENE SURFACE

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In recent years, a considerable amount of attention has been devoted to understanding the interaction and dynamics of water molecules on carbon-based surfaces, such as graphene and polycyclic aromatic hydrocarbons (PAHs), due to their importance in a variety of chemical and physical phenomena [1], including ice nucleation [2], catalysis, separation technologies [3], atmospheric chemistry, interstellar dust grain chemistry [4], and others. Molecular level insights on the interactions on carbon surfaces is essential to understanding these processes. However, studying microsolvation dynamics of large PAHs poses several experimental and theoretical challenges.

In this work, we used broadband rotational spectroscopy in the 2-8 and 2-18 GHz range under the cold and isolated conditions of a supersonic jet expansion to investigate how a single water molecule binds and moves on a pyrene surface. Pyrene is a planar four ring PAH that begins to mimic the conditions that are found in graphene. The observed rotational spectrum of the pyrene-water complex exhibits characteristic line splittings arising from internal dynamics that are notably complex, making spectral analysis particularly challenging. The observed tunneling splittings were analyzed with auxiliary quantum chemistry calculations, suggesting that the water motion across the carbon surface proceeds primarily through a tunneling motion involving its translation between the two equivalent aromatic rings furthest from the center of mass of pyrene and the presence of another tunneling motion related to the rotation of the water molecule about its C_2 symmetry axis. This is a similar behavior to what is reported for the phenanthrene-water complex [5]. However, we identify an additional splitting that is absent in mono-hydrated phenanthrene, suggesting that the pyrene-water complex, due to its higher symmetry, creates the possibility for multiple equivalent tunneling pathways which might couple and interfere with each other.

In this contribution we will discuss our theoretical strategies for identifying the possible tunneling pathways and predicting the complex splitting patterns observed for the water-pyrene complex.

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Acknowledgements:

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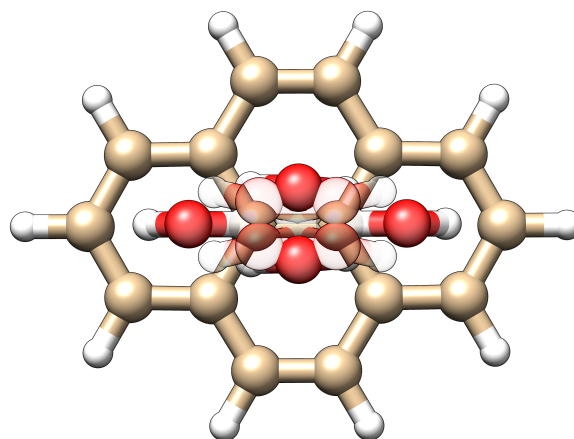


Figure 5: Two possible and equivalent tunneling pathways for the water molecule.

MICROSOLVATION OF WATER BY CO₂: THE STUDY OF WATER-(CO₂)_n BY QUANTUM CHEMISTRY AND ROTATIONAL SPECTROSCOPY, WITH UP TO $n = 5$

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The precise characterization of weak intermolecular interactions between water and carbon dioxide molecules is important to better understand binary nucleation problems, such as the formation of H₂O and CO₂ ice clouds in the atmosphere of Mars.¹ It was recently found that the presence of CO₂ accelerates the nucleation of water at low temperature due to the formation of short-lived heterodimers.² We investigate here the formation of larger mixed water-CO₂ clusters formed in a supersonic jet expansion and probed with a recently developed 2–18 GHz chirped-pulse Fourier transform microwave spectrometer.

Possible structures for the most stable isomers were first identified with a CREST conformational search and then geometry optimized with DFT and *ab initio* methods. Considering our highly congested experimental spectra, accurate predictions of the rotational constants were not sufficient for assignment, and we thus implemented a recently developed extended cross correlation method:³ two spectra recorded under the same conditions except for CO₂ concentration provide subsets of intensity ratios that correlate with cluster sizes. In total, we identified four new isomers, each observed for both H₂O and D₂O: one isomer of water-(CO₂)₃, two almost isoenergetic isomers of water-(CO₂)₄, and one isomer of water-(CO₂)₅. The assignment of the water-(CO₂)₅ isomer was guided by the ground-state parameters recovered from a previously assigned infrared spectrum measured in Calgary. The two water-(CO₂)₄ isomers have distinct symmetries, one with a plane of symmetry (C_s) and the other with a two-fold rotational axis (C_2). The latter was established directly from the spectrum, through the 1:3 (2:1) intensity alternation following the K_c parity due to the nuclear spin statistics of the H₂O (D₂O) subunit.

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C-II: Contributed Talks

Monday, August 31, 2026, 14:00

Chair : Brooks H. Pate

AII

SEQUENTIAL CAVITY-MODE AUTO-LOCK SPECTROSCOPY (SCALS) OVER HUNDRED-TERAHERTZ RANGE WITH KILOHERTZ PRECISION

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Precision spectroscopy of narrow optical transitions underpins modern metrology and fundamental physics, yet a fundamental trade-off between frequency accuracy and scan speed has long constrained the field. Here we demonstrate a cavity-enhanced spectroscopic method, termed SCALS (Sequential Cavity-mode Auto-Lock Spectroscopy), that overcomes the traditional trade-off between scanning speed and precision by implementing a dual-loop Pound-Drever-Hall locking scheme combined with sequential cavity-mode auto-locking, real-time optical frequency comb calibration, and automated data acquisition. Our system achieves continuous frequency scans spanning hundreds of terahertz with kilohertz-level absolute frequency accuracy, at instantaneous scan rates up to 30 MHz/s. The key enabling feature is a cyclic lock-scan-unlock-relock sequence that sequentially steps the locking point from one cavity mode to the next, enabling unattended, automated operation over extended periods.

We validate the instrument on C₂H₂ lines around 1542 nm, agreeing with BIPM-recommended values within uncertainty. We then demonstrate broadband saturated absorption spectroscopy of CH₄ and HDO over 5900–6140 cm⁻¹, resolving thousands of sub-Doppler transitions including previously unpredictable two-photon features. This work enables, for the first time, exploratory precision spectroscopy of polyatomic molecules without a priori knowledge of transition frequencies, opening new avenues for various studies.

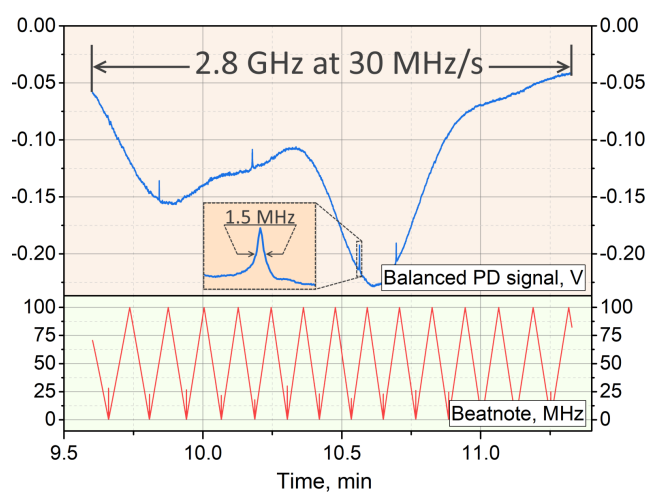


Figure 6: A piece of SCALS spectrum of CH₄

HIGH-EFFICIENCY LASER SPECTROSCOPY ON COLD RADIOACTIVE MOLECULES USING CONTOURED NOZZLES

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Laser spectroscopy studies of radioactive molecules have been proposed owing to their enhanced sensitivity to the nuclear Schiff moment, which probes physics beyond the standard model (e.g. $^{227,229}\text{ThO}$, ^{227}AcF , $^{229}\text{PaF}^{3+}$), as tracers for astrophysical processes (e.g. ^{26}AlF) [1] or to investigate their magnified nuclear effects such as e.g., nuclear magnetization in ^{225}RaF [2]. Precision experiments of such radioactive molecules are often hindered because of the limited knowledge of their electronic structure, half-lives as short as a day (e.g. ^{229}Pa) and the large number of rovibrational states populated when those isotopes are produced directly at accelerator facilities in microscopic quantities [3].

Hypersonic gas jets are ideal to study the hyperfine structure of short-lived actinides (100's ms) produced in only several atoms per second, e.g. $^{254(m)}\text{No}$ [4] at GSI. Produced using fusion-evaporation reactions at accelerator facilities, these actinides are stopped in a gas cell with continuous argon flow. The in-gas-jet method then relies on a contoured de Laval nozzle to create a cold, long and well-collimated argon jet with an almost uniform Mach number of around 8.5. Laser spectroscopy with resolutions of around 200 MHz (FWHM) are achieved in the gas jet for typical (near) UV transitions in actinides [5]. We present here the first characterization and application of the in-gas-jet laser ionization and spectroscopy method to radioactive molecules that was conducted at KU Leuven. Translational and rotational temperatures in the hypersonic gas jet were determined via laser spectroscopy of ^{232}ThO to be around 12 K and 7 K respectively along the full 60 mm gas jet. An upper bound of the vibrational temperature was estimated as no transitions from $v'' = 1$ were observed. Laser ablation of salt-based ^{230}ThO and ^{229}ThO targets containing micro-grams of material was performed in a room-temperature argon-filled gas cell. Preliminary molecular King-plot analysis shows an enhanced sensitivity to the field shift (nuclear volume) compared to earlier studies and limited isotopologue dependence on the rotational constants. To push the resolution of the technique to the kHz regime, RF excitation has already been implemented at KU Leuven [6] and microwave excitation will be implemented in a new gas jet setup currently being designed at the Facility for Rare Isotope Beams (FRIB) at Michigan State University, where a different production mechanism will extend the technique to radioactive molecules containing neutron-rich isotopes.

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HIGH-PRECISION SPECTROSCOPY OF H_2^{16}O : IMPROVING THE SPECTROSCOPIC NETWORK THROUGH LAMB DIP AND TWO PHOTON ABSORPTION NICE-OHMS MEASUREMENTS

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Water is a critical molecule in chemistry and radio astronomy, and is a benchmark species for molecular spectroscopy for which multiple databases and spectroscopic networks exist¹². Our work demonstrates how high-precision, Doppler-free measurements—achieved via wave-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS³) can be strategically integrated to refine the entire spectroscopic network.

To enhance the accuracy of protected radio lines between 750 GHz and 3 THz, we performed Lamb-dip measurements of rovibrational lines in the 1.2–1.4 μm range. Achieving a precision of ≤ 2 kHz, these near-infrared measurements were added to the network to improve the precision on 51 purely rotational microwave lines⁴. As a result, the precision of these transitions, formerly sitting at the 10–200 kHz level, has been reduced to well below 10 kHz across all lines.

Furthermore, we expand the network’s reach into high-energy states by reporting the first-ever two-photon absorption (TPA) measurements in the water overtone range, resolved with kHz accuracy⁵. These high-precision TPA measurements, allowing for parity-conserving transitions, provide anchors to the spectroscopic network in the high energy domain, thus improving the entire network with only a few well chosen transition measurements.

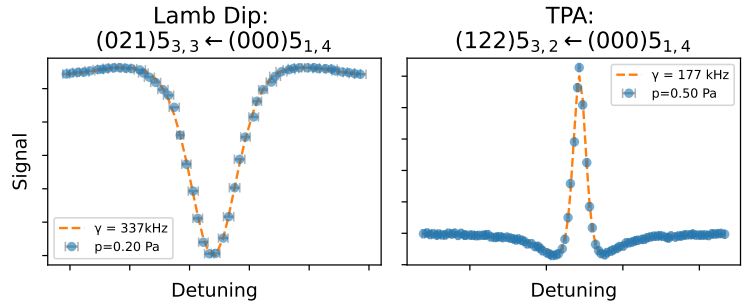


Figure 7: H_2^{16}O spectra measured with our ultrasensitive NICE-OHMS set-up. Left panel: Experimental Lamb-dip spectrum, Right panel: Experimental two-photon absorption spectrum.

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SINGLE-PHOTON DOPPLER-FREE SPECTROSCOPY IN THE VACUUM AND EXTREME ULTRAVIOLET

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The ionisation energies of many atoms and molecules lie in the vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) regions of the electromagnetic spectrum, which correspond to wavelengths shorter than 200 nm and 105 nm, respectively. Laser radiation generated at these wavelengths is therefore needed when performing single-photon excitation from the ground electronic state of an atom or molecule to highly excited electronic states. However, although VUV/XUV laser sources with < 250 MHz bandwidths have been demonstrated,¹²³⁴⁵ large Doppler broadening of transitions in the VUV/XUV often limit the achievable resolution of single-photon VUV/XUV spectroscopy, even for samples in skimmed supersonic beams. Additionally, systematic Doppler shifts of > 100 MHz can affect VUV/XUV transition frequencies if the VUV laser and supersonic beams do not cross at exactly 90°.

Here, we demonstrate a technique for achieving sub-Doppler linewidths, with laser-limited full-widths at half maxima of < 20 MHz in the VUV/XUV spectral regions. This technique is based on the combination of a Doppler-free imaging-assisted detection scheme for single-photon transitions⁶ with a long-pulse-length (~ 50 ns) Fourier-transform-limited pulsed XUV laser. Sub-Doppler resolution can be achieved by exploiting the correlation, in pulsed supersonic expansions, between the transverse velocities and the positions of the absorbing molecules. By performing (1 + 1') resonance-enhanced two-photon ionisation spectroscopy of the $(4p^6) ^1S_0 \rightarrow 6s'[^2P_{1/2}]_{J=1}$ transition of Kr at ~ 95 nm, we observed these position-dependent Doppler shifts by imaging the ions (see spectra in the left column of Figure 1). Retroreflection of the XUV laser from a B₄C mirror resulted in the inversion of the observed Doppler shifts and enabled the residual first-order Doppler shifts to be precisely measured and compensated. Summing the spectra obtained at different detector regions, after correction of the first-order Doppler shifts, enabled the detection of the first purely Doppler-free single-photon spectra in the VUV/XUV region (see spectrum in the right column of Figure 1). The increased single-to-noise ratio of this spectrum illustrates the power of this new technique.

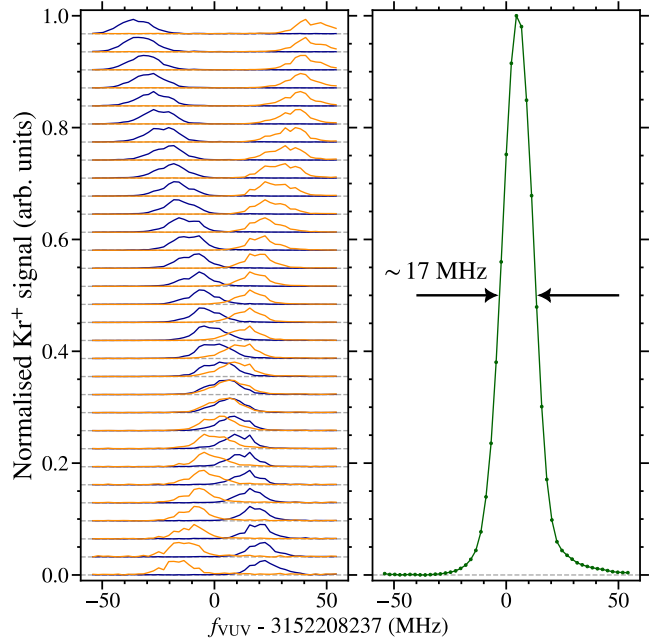


Figure 8: (Left) Spectra of the $(4p^6) ^1S_0 \rightarrow 6s'[^2P_{1/2}]_{J=1}$ transition in Kr recorded at different spatial positions in a supersonic expansion using ion-imaging techniques. The spectra obtained with the incident and retroreflected XUV laser beams are displayed in blue and orange, respectively. (Right) Spectrum obtained by summation of the spectra recorded at different detection positions after correcting for the measured Doppler shifts.

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TOWARDS HIGH RESOLUTION SPECTROSCOPY IN THE FAR-INFRARED RESTSTRAHLEN GAP USING NONLINEAR METASURFACE FOR DIFFERENCE FREQUENCY GENERATION

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The availability of narrow-linewidth, widely tunable, and high-power radiation sources is essential for high-resolution molecular spectroscopy. Despite decades of instrumental developments, such sources remain unavailable in the far-infrared (2–20 THz) spectral region. Here, we demonstrate a new far-infrared difference-frequency generation spectrometer based on giant nonlinear-response metasurfaces. The instrument provides μW -level signal, high spectral resolution, and continuous frequency coverage from 7 to 10 THz, a range that remains totally inaccessible to quantum cascade lasers because of Reststrahlen-band absorption in available semiconductor materials.

Two continuous-wave mid-infrared laser beams were employed to generate THz radiation via difference-frequency generation on the metasurface. Those lasers, operating at wavelengths of 10 μm and 8 μm were combined and focused on the metasurface where their frequency difference that lays in the THz range was generated. This THz radiation is collected with the parabolic mirror and later on exploited for the spectroscopic measurements. In this presentation, I will give details of this new experimental set-up, as well as its capabilities for high resolution THz molecular spectroscopy using the recently recorded spectra of H_2O , NH_3 , CH_3OH , and NH_2 radical.

ABSORPTION SPECTROSCOPY MEETS THE ACCURACY OF PURELY FREQUENCY-BASED DISPERSION SPECTROSCOPY

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A wide range of high-accuracy spectroscopic applications such as, greenhouse-gas monitoring, isotope-ratio analysis, optical thermometry, primary gas standards, validation of molecular-collision models as well as quantum electrodynamical calculations require precise measurement of spectral line shapes and intensities at per mil (‰) level. Cavity ring-down spectroscopy (CRDS) [1] is particularly well suited in this context due to its high sensitivity, precision (below 0.01‰) and calibration-free operation; however, its accuracy is often limited to several percent due to inaccuracies in light intensity measurements [2,3,4].

While ongoing advances in laser-frequency and cavity-length stabilization, together with the use of optical frequency combs, have significantly improved the precision and accuracy of the horizontal (frequency) axis, the intensity based vertical axis (absorption coefficient) remains susceptible to insufficient linearity and bandwidth of detection system, including the detector, digitizer, and associated electronics. This distortion in the detection band causes the measured decay curve to deviate significantly from an ideal exponential, leading to incorrect fitted time constants and structured, non-random fit residuals.

To overcome this problem, we developed a correction methodology in which the transfer function (TF) of the complete detection system is measured using heterodyne detection of two frequency-detuned laser beams. An analytical expression for the TF was derived and validated against numerous experimentally measured TFs obtained with different detection systems. This analytical TF is then incorporated into the ring-down fitting routine via Fourier convolution. This approach enables more accurate extraction of decay time constants without requiring any modifications to the existing CRDS setup.

We validate our TF corrected CRDS (TF-CRDS) method using the CO R(23) 3–0 transition, achieving line-intensity accuracy at the per mil level, in agreement with independent spectroscopic techniques such as cavity mode dispersion spectroscopy (CMDS) [5,6] and heterodyne cavity ring-down spectroscopy (HCRDS) [4] which are inherently immune to detection system nonlinearities. Thus, correcting for detection system nonlinearity enables conventional CRDS to reach accuracy levels previously attainable only with more advanced techniques [3, 4, 5, 6], making it a competitive tool for high-accuracy optical gas metrology.

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PHASE-COHERENT CP-FT THZ EMISSION SPECTROSCOPY WITH A NBN HOT ELECTRON BOLOMETER

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The chirped-pulse Fourier transform (CP-FT) emission spectrometer developed at the PhLAM laboratory [1] operates over the 0.05–0.5 THz frequency range. A key feature of the instrument is the use of a direct digital synthesizer (DDS) at the first stage of the frequency multiplication chain. The DDS generates both single-frequency excitation pulses and frequency-chirped excitation pulses with high phase stability and flexibility. Another distinctive characteristic of the spectrometer is the use of the same THz source for both molecular excitation and signal detection. During signal detection, the source also serves as the local oscillator of the heterodyne receiver. The original receiver employs a fundamental Schottky-diode mixer. This architecture simplifies the spectrometer and enables phase-coherent detection. As a result, coherent averaging can be performed directly in the time domain over extended acquisition times.

To further increase the sensitivity of the instrument, we are currently evaluating a niobium nitride (NbN) hot electron bolometer (HEB) as a replacement for the Schottky mixer. The NbN HEB has an intrinsically broad intermediate-frequency bandwidth of several tens of gigahertz [2]. It can therefore operate as a fundamental heterodyne mixer and provides substantially higher sensitivity. We will present the first experimental results obtained with the NbN HEB integrated into the PhLAM CP-FT emission spectrometer in the 0.4–0.5 THz frequency range. We will also discuss the prospects for extending the same phase-coherent detection architecture beyond 1 THz by using the NbN HEB receiver.

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2. G. Torrioli, A. Forrer, M. Beck, et al. *Opt. Express* 31, 15942-15952 (2023).

MASER REFERENCED DISPLACEMENT SENSOR

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¹Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Louvain-la-Neuve, Belgium

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Inertial sensors are essential tools for gravitational-wave detectors. These detectors typically rely on Fabry-Pérot cavities that are actively stabilized to minimize mechanical noises in the frequency range of interest. This stabilization demands precise monitoring of the mirrors motion using displacement sensors. Various techniques have been developed for such inertial sensing, achieving impressive sensitivities using Fabry-Pérot cavities¹ or Michelson interferometers²³.

Heterodyne cavity tracking relies on measuring the beating between two optical cavities. The stability of each cavity impacts the precision of

this measurement since it involves a relative motion between the two cavities. In this talk, we present proof of concept for a new method for heterodyne inertial sensing that enables absolute displacement measurement. Using an optical frequency comb beating separately with two optical cavities, we can eliminate common-mode noise from the reference oscillator, effectively forming a balanced inertial sensor. With this method, we reach a sensitivity of $700 \text{ fm}/\sqrt{\text{Hz}}$ at 1 Hz, close to the state-of-the-art of $260 \text{ fm}/\sqrt{\text{Hz}}$, and $10 \text{ fm}/\sqrt{\text{Hz}}$ at 1 kHz¹.

A projected two-orders of magnitude improvement in sensitivity will be discussed along with its potential applications in gravitational waves detectors.

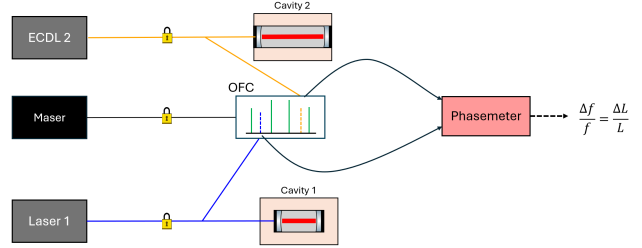


Figure 9: Scheme for the experimental setup. ECDL: External Cavity Diode Laser, OFC: Optical Frequency Comb.

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C-III: Contributed Talks

Monday, August 31, 2026, 14:00

Chair : Jer-Lai Kuo

B11

WMS-ROT: FROM QUANTUM-CHEMICAL CALCULATIONS TO ASSIGNMENT-READY ROTATIONAL SPECTRA

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Reliable prediction and assignment of high-resolution rotational spectra require accurate spectroscopic parameters: equilibrium geometries, harmonic force fields, and anharmonic corrections, typically at the VPT2 level [1], including recent efficiency improvements [2]. Their combined accuracy is essential to reach deviations of about 0.1% in rotational constants. Rotational spectroscopy is therefore a stringent benchmark for molecular structures, since small residual errors in geometries or vibrational corrections directly affect predicted spectra. Standard tools such as SPCAT and SPFIT [3] are reliable but require specialized expert.

In this contribution, we present WMS-Rot [4], the rotational component of the Web Multifrequency Spectrometer, designed to streamline prediction and assignment from high-quality quantum-chemical data. The workflow relies on Pisa Composite Schemes, including PCS2 and BDPCS3 [5,6], and supports interactive spectrum simulation, visualization, and local refinement through WMS-FitRot. WMS-Prep further automates parsing of Gaussian output files and converts centrifugal-distortion constants between representations [7]. Browser-side execution via WebAssembly and Pyodide enables these Python-based workflows without installation or compilation.

Applications to nicotinic acid and thiopronine show that composite quantum-chemical inputs combined with assignment-aware refinement enable reliable conformer discrimination and assignment-ready predictions while preserving compatibility with Pickett-style Hamiltonians and SPCAT/SPFIT workflows.

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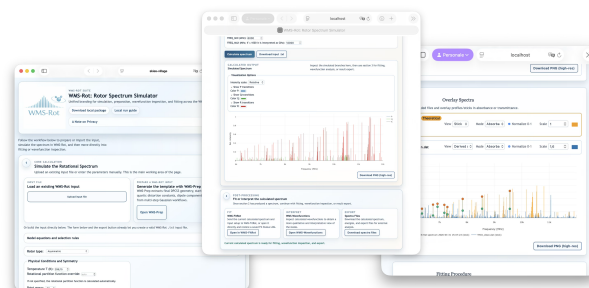


Figure 10: The WMS-Rot webpage

MACHINE-LEARNING CALIBRATION OF ROVIBRATIONAL ENERGY LEVELS OF CO₂ ISOTOPOLOGUES

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Accurate rovibrational energies for CO₂ isotopologues are needed for atmospheric retrievals, greenhouse-gas monitoring, planetary modeling, and high-temperature radiative transfer. We introduce a residual machine-learning correction for twelve stable CO₂ isotopologues¹ trained on empirically-derived MARVEL energies² using Ames-2021² and CDSD-296³ as physics-based baselines. The model learns $\Delta E = E_{\text{MARVEL}} - \frac{1}{2}(E_{\text{Ames}} + E_{\text{CDSD}})$, preserving calculated structure while correcting experiment-theory disagreement.

A compact LightGBM model⁴, using quantum numbers (J, v_1, v_2, v_3, r, p) and two Ames-CDSD disagreement descriptors, was tested by leave-one-isotopologue-out validation. For 50,258 MARVEL-matched levels, it reaches a weighted MAE of 0.00165 cm^{-1} , improves every withheld isotopologue, and approaches CDSD-296 accuracy (0.00145 cm^{-1}). It also calibrates 486,309 calculated levels without MARVEL counterparts.

Robustness was tested by injecting artificial errors simulating coherent band shifts, sparse random noise, and dense random noise. All scenarios show strongly sublinear degradation even for injected errors up to 150 cm^{-1} . Worst-case systematic degradation remains below 0.2 cm^{-1} ; random coherent errors plateau near 0.028 cm^{-1} , and sparse zero-mean errors near 0.004 cm^{-1} . Thus, the model does not transfer small or large training errors and can indicate spectroscopic regions needing inspection.

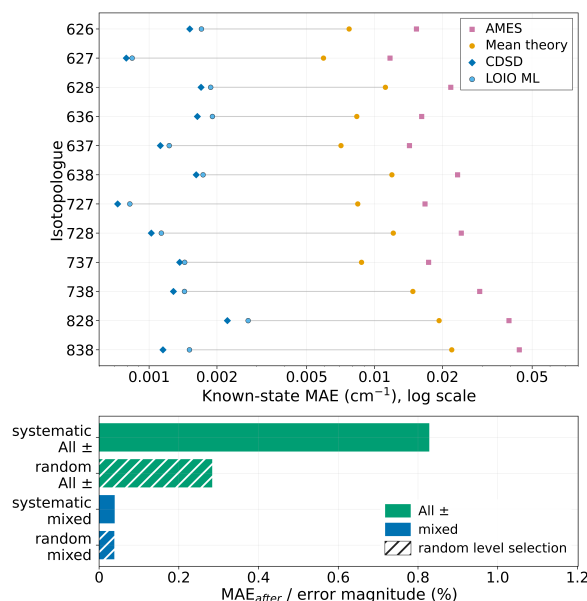


Figure 11: Top: known-state MAE for Ames, CDSD, mean theory and LOIO-ML. Bottom: error-normalized MAE after 10 cm^{-1} injections; hatching denotes random selection.

$$MAE = |E_{\text{MARVEL}} - E_{\text{ref}}|$$

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ACETAMIDE: A STRANGE BREW OF STRUCTURE, SPECTROSCOPY AND THEORY

Terri E. Field-Theodore¹, Nicolò Quaresima², and Peter R. Taylor³

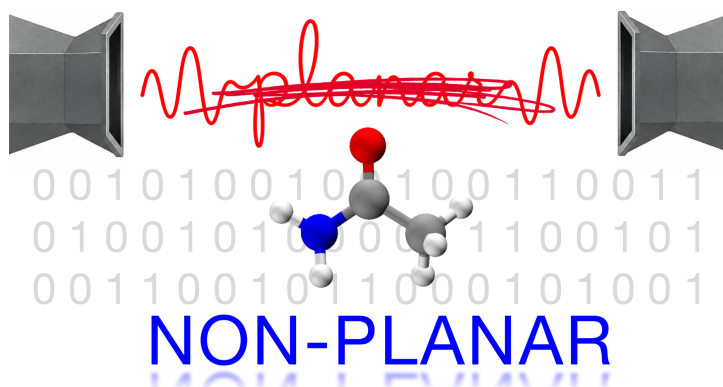
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The importance of acetamide in prebiotic chemistry and structural biology is well established. Possessing a peptide bond with characteristic resonance, it is expected on chemical grounds to adopt a planar framework (aside from the methyl hydrogens). Spectroscopy supports this assignment, yet high-level quantum chemical calculations predict a non-planar minimum. In this work, we show that this apparent contradiction originates from the topology of the underlying potential energy surface, not from deficiencies in either experiment or

theory. Coupling between CH₃ rotation and NH₂ inversion generates a multidimensional landscape in which the vibrationally averaged structure appears planar, despite being a non-planar equilibrium geometry. Our results further suggest that large-amplitude NH₂ torsional motion may account for the experimentally observed absence of a *c*-dipole component. The implications of this work extend to flexible molecules containing amino, amide and methyl functional groups in chemical, biological, and astrochemical contexts, where such effects play a central role in determining structure and spectroscopy.



NEW 4TH ORDER PARAMETER DEFINITIONS AND BRUTE FORCE APPROACH TO THE CONTACT TRANSFORMATION FOR THE G_6 TORSION-ROTATION PROBLEM

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¹Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France

This work aims to provide initial starting parameters and recommended reductions for the torsion-rotation Hamiltonian for methanol-like (G_6) molecules up to fourth order. At present, few of the fourth order terms have been defined, many of them assuming the absence of torsion and an accepted approach to reducing the Hamiltonian is absent. Experimental spectroscopists are thus left with a large-scale “guessing game” as to decide which operators to include and what values to use as the starting parameters. Having fourth order parameter values and suggested reductions *a priori* would heavily smooth the process from the initial simulation to the final fit. The new proposed definitions for the fourth order kinetic terms follow a variation of the τ_{ijkl} centrifugal distortion parameters relying instead on the 4×4 inertial tensor to explicitly include the torsional momentum and then summing over the non-torsional vibrational modes. These are accompanied by the Fourier expansion of the inverse inertial tensor to provide the $\sin 3\alpha$ and $\cos 3\alpha$ dependent torsion-rotation terms. Applying a Watson-style contact transformation to this Hamiltonian results in over 130 million possible reductions. Since this is far too many to manually test for a given molecule, a brute force strategy for determining likely reasonable reductions is proposed. Every possible reduction is calculated and the norm-2 of the vector of reduction parameters is then stored. The reductions with the lowest norms are assumed to be more valid guesses and a collection of them is then printed as possible starting points. These efforts are collected into two numerical recipes: the first is for processing *ab initio* calculations to predict these parameters and the second to perform the reduction as a means of providing a more confident initial simulation of a torsion-rotation spectrum.

HIGH-TEMPERATURE RAMAN SPECTRA OF CO₂ ISOTOPOLOGUES: MODELING WITH AN INTERACTING ANHARMONIC OSCILLATOR APPROACH

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Computing spectroscopic observables, such as line positions and intensities, provides a valuable test of vibrational models. In particular, Raman spectroscopy enables the characterization of isotopologue mixtures through their spectral signatures. Recent experimental studies have provided Raman transition moments for several CO₂ isotopologues, allowing direct comparisons between theoretical predictions and measured spectra up to 2000 K. However, a systematic description of Raman signatures across the complete series of CO₂ isotopologues remains limited. In this study, we investigate the spectra of the CO₂ isotopologues using an effective Hamiltonian model incorporating interacting Morse oscillators for the stretches and an anharmonic $U(3)$ basis for the bending mode. From the resulting vibrational wave functions, we compute transition moments of the mean polarizability, represented as an expansion in curvilinear coordinates up to cubic terms. The polarizability surface is fitted to reproduce 90 experimental transition moments measured for four isotopologues. Pure vibrational simulations are extended to include rotational effects through the vibrationally dependent rotational constants B_ν , improving the calculated intensities. The simulated spectra are compared with available experimental data, including high-resolution measurements of all twelve stable CO₂ isotopologues obtained in our group, showing consistent agreement with experimental observations. This approach may provide a foundation for the quantitative determination of relative isotopologue abundances in CO₂ mixtures from Raman intensities.

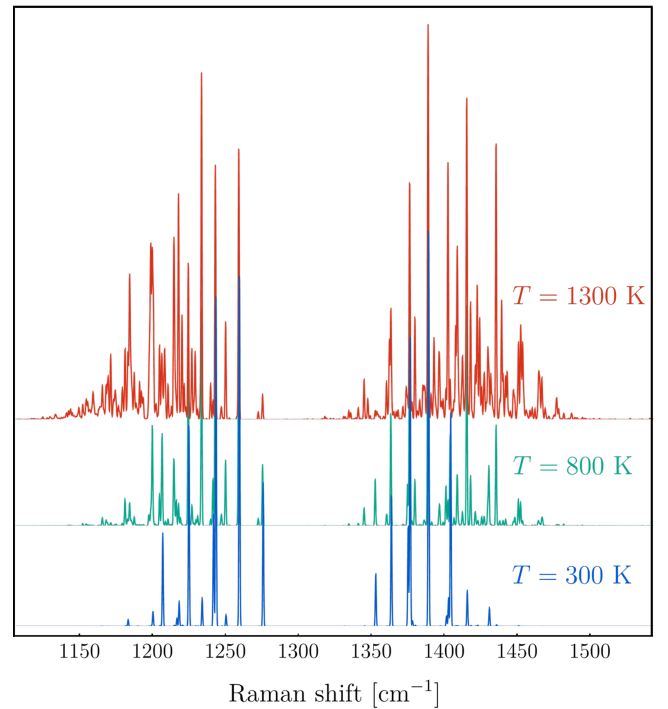


Figure 12: Simulated vibrational Raman spectra of a CO₂ isotopologue mixture containing six ¹²C-based isotopologues with oxygen atoms from ¹⁶O, ¹⁷O, and ¹⁸O. Relative abundances correspond to the composition of a sample measured by our group.

AB INITIO COLLISION-INDUCED LINE SHAPE PARAMETERS FOR AIR-PERTURBED R(0) 0-0 LINE IN HF

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Hydrogen fluoride, along with other hydrogen halides, plays a crucial role in quantitative atmospheric and astrophysical spectroscopy. In particular, these species are heavily involved in stratospheric ozone depletion chemistry [1]. However, to be applicable in atmospheric science, the spectra of terrestrial hydrogen halides must be considered in the presence of the surrounding N₂ and O₂ molecular bath. We present the first fully quantum mechanical scattering calculations of collision-induced line-shape parameters for both the O₂- and N₂-perturbed R(0) 0-0 line in HF. For the N₂-perturbed case we use the full-dimensional ab initio potential energy surface (PES) from [2], and for the O₂-perturbed case our calculations are based on a new, highly accurate 4-dimensional PES. The close-coupling scattering calculations were carried out using BIGOS, an in-house computational package developed in our group [3].

The obtained scattering *S*-matrices were used to calculate the spectroscopic cross sections, from which the temperature-dependent line-shape parameters—including pressure broadening, pressure shift, and the complex Dicke parameter—were derived. Moreover, a comparative analysis of the potential surfaces of these two systems offers insight into the intermolecular interactions driving the collisional effects, highlighting the key dependence of the cross sections on both the anisotropy and long-range behavior of the potential.

Combined with the previously reported results by Chai *et al.* [4] for Ar, the third most abundant constituent of Earth's atmosphere, these calculations provide a comprehensive set of collision-induced line-shape parameters for HF perturbed by air. This work can serve in populating the spectroscopic databases and in providing a reference for future experimental works.

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RECENT ADVANCES IN HIGH-RESOLUTION SPECTROSCOPY OF ASTROPHYSICALLY IMPORTANT DIATOMIC MOLECULES

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²Department of Physics and Astronomy, University College London, London, UK

Progress in the high-resolution spectroscopy of astrophysically important diatomic molecules is presented. The work combines high-level *ab initio* electronic structure calculations, variational nuclear-motion calculations, and MARVEL (Measured Active Rotational–Vibrational Energy Levels) analysis to investigate the spectroscopy of HF [1], OH [2], and CO [3, 4, 5]. The studies include the HF $B^1\Sigma^+ - X^1\Sigma^+$ and $C^1\Pi - X^1\Sigma^+$ band systems, the OH $B^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ band systems, and several bands of the CO molecule.

The resulting datasets include accurate transition frequencies, line intensities, Einstein coefficients, radiative lifetimes, absorption cross sections, rovibronic line lists, and empirical energy levels. For HF and CO, MARVEL energy levels are incorporated into the refinement of the spectroscopic models, while for OH they provide an independent benchmark for validating the theoretical predictions.

These studies demonstrate the capability of modern theoretical and empirical spectroscopic methodologies to produce reliable spectroscopic data for molecules of astrophysical interest while providing comprehensive datasets where experimental information remains scarce. The resulting line lists and spectroscopic datasets contribute to ongoing efforts in high-resolution molecular spectroscopy and support applications in atmospheric science, planetary atmospheres, exoplanet characterization, and astrophysical spectral modelling.

This work represents a collaborative effort involving researchers from Khalifa University, University College London (ExoMol), and international collaborators.

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VIBRATIONAL-ROTATIONAL SPECTROSCOPIC CHARACTERIZATION OF THE INTERSTELLAR COMPLEX ORGANIC MOLECULE METHYL ACETATE

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Methyl acetate ($\text{CH}_3\text{COOCH}_3$), the simplest saturated ester, was first detected in the molecular cloud Orion KL in 2013 (Tercero, et al., *Astrophys. J. Lett.* 770, L13, 2013), and very recently confirmed toward the Galactic Center molecular cloud G+0.693. Being the second most stable species within the $\text{C}_3\text{H}_6\text{O}_2$ isomeric family (Sanz-Novó, et al., *Astron. & Astrophys.* 706, A316, 2026), methyl acetate is a complex organic molecule (COM) of particular interest in astrochemistry due to its potential involvement in the reaction mechanisms that lead to the formation of ester-bearing molecules and prebiotic species, both in icy mantles and warm gas of the interstellar medium (ISM). Given this importance, its spectroscopic characterization is therefore crucial to contribute to the spectroscopic databases that might help observation in the interstellar gas and ices. In the present work, the vibrational and ro-vibrational properties of methyl acetate are studied by state-of-the-art quantum chemical calculations. Equilibrium geometries and harmonic frequencies are computed by CCSD(T) based composite schemes (Puzzarini, et al., *Chem. Rev.* 119, 13, 2019), which are then augmented through anharmonic contributions evaluated in the frame of the density functional theory. From this hybrid force field, excited state rotational constants, vibrational transition frequencies and absorption intensities are worked out by resorting to vibrational second-order perturbation theory. Simulated spectra were used to assist the analysis of the gas-phase infrared (IR) spectrum, recorded in the 150-6500 cm^{-1} region at a resolution of 0.5 cm^{-1} by using a Bruker Vertex 80v equipped with a 199 mm cell with polyethylene and KBr windows for the far- and medium-IR region, respectively. Finally, the full characterization of the IR features was completed with the experimental determination of absorption cross sections over the same region, by using spectra acquired at sample pressures in the 9 – 100 hPa range.

D: Posters

Monday, August 31, 2026, 16:30

FUNDAMENTAL INVARIANT NEURAL NETWORKS APPLIED TO THE SPECTROSCOPY OF PROTONATED ACETYLENE

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Machine learning (ML) is a rapidly growing field in physics and chemistry.¹ ML methods include using neural networks (NN) which are trained with *ab initio* molecular energies so as to obtain multidimensional molecular potential energy surfaces.²

ML will be applied to the non-rigid protonated acetylene (C_2H_3^+) species in order to derive a potential energy surface compatible with its large amplitude migrational motion.³ An NN will be trained with a dataset consisting of molecular configurations with their *ab initio* energies. Symmetry, which is crucial in this molecule,⁴ requires that the potential energy surface be invariant under interchange of the hydrogen and carbon atoms. This requirement is fulfilled thanks to Fundamental Invariants⁵ (FI) which, as shown in Figure 1, are used as input for the neural network instead of the internal coordinates. Upon training, the NN model allows us to compute molecular energies for any configuration. The energy gradient and Hessian can be analytically retrieved as well. The NN model is used to retrieve many important results concerning protonated acetylene while accounting for its large amplitude migrational motion.⁴ One of the first results are reference positions $\mathbf{a}_i(\alpha)$ which are atom trajectories during the large amplitude migrational motion. The migrational potential energy function, with the zero-point energy contribution, can be calculated as well using the Hessian. The reference positions along with the migrational potential allow us to compute many spectroscopic properties including the migrational tunneling energies and the migrational spectrum. This spectrum, which should be observed in the far infrared domain, has not been recorded yet. Other spectroscopic results include vibrational energies and the migrational tunneling splitting for excited vibrational energies.

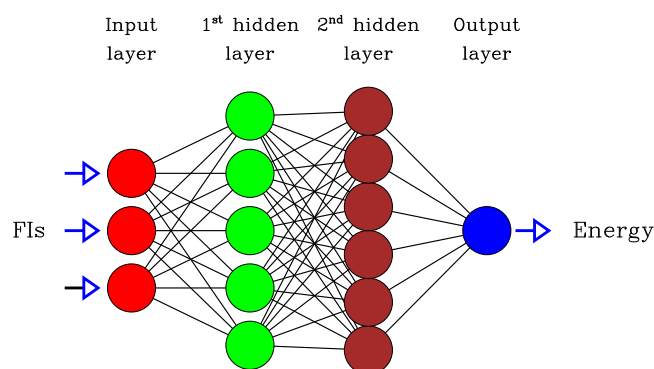


Figure 13: Functional structure of the NN used for fitting the PES of protonated acetylene with FIs in the input layer and the energy in the output layer.

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²Schmitz *et al.*, *J. Chem. Phys.* **150** (2019) 244113

³Weber, Yohsimine, and McLean, *J. Chem. Phys.* **64** (1976) 4159

⁴Hougen, *J. Mol. Spectrosc.* **123** (1987) 197; Escibano and Bunker, *J. Mol. Spectrosc.* **122** (1987) 325; and Escibano *et al.*, *Chem. Phys. Lett.* **150** (1988) 60

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THE ELECTRON SPIN-ROTATION-TORSION HAMILTONIAN ACCOUNTING FOR DISTORTION EFFECTS

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Distortion effects will be added to the electron spin-rotation-torsion Hamiltonian derived recently to model the spectrum of open shell $^2\Sigma$ molecules displaying a large amplitude torsional motion of their methyl group and to describe the electron spin-torsion coupling.¹

The approach parallels those of Watson,² Brown and Sears,³ and Nakagawa *et al.*⁴ In a first step, an unreduced Hamiltonian is built adding all the terms which are symmetrical and invariant under time reversal. This Hamiltonian is reduced in a second step removing unwanted or indeterminate terms with the help of contact transformations.

The unreduced Hamiltonian is written as the sum of products of an electron spin-rotation operator and a torsional operator. The electron spin-rotation operators were determined by Brown and Sears³ and involve molecular fixed components N_α and S_β of the rotational and electron spin angular momenta. The torsional operators can be found in Nakagawa *et al.*⁴ Parameterizing the torsional motion with the angle γ , these operators are expressed in terms of $\cos 3q\gamma$, $\sin 3r\gamma$, and p_γ the momentum conjugate to γ .

The order 2 unreduced Hamiltonian thus built contains a total of 15 terms including 8 rotation-torsion, 5 electron spin-rotation, and 2 electron spin-torsion terms. Compared to the electron spin-rotation-torsion Hamiltonian previously derived,¹ this unreduced Hamiltonian contains an additional term in $p_\gamma N_x$.

The order 4 unreduced Hamiltonian contains a much larger number of terms equal to 75. 9 terms in $\cos 3\gamma\{N_\alpha, S_\beta\}$ and $\sin 3\gamma\{N_\alpha, S_\beta\}$ arise and describe a torsional dependence of the electron spin-rotation coupling. The unreduced Hamiltonian also contains a term in $p_\gamma S_y$ not found in the electron spin-rotation-torsion Hamiltonian¹ for symmetry reasons. This term, $\{\sin 3\gamma, p_\gamma\}S_y$, describes distortion effects for the electron spin-torsion coupling

The next step of the contact transformation requires building a unitary operator U equal to $\exp(iS)$, where S changes sign under time reversal and is also written as a sum of products. S is written as 8 order 1 and 9 order 3 terms which should allow us to remove up to 17 terms in the unreduced Hamiltonian.⁴

The analysis of the newly assigned transitions of the acetyl radical (CH_3CO) will also be presented. Hopefully the 1100 transitions available now for $v_t = 0$ and 1 will be analyzed with the present new fitting Hamiltonian.

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²Watson, *J. Chem. Phys.* **46** (1967) 1935; and Watson, *J. Chem. Phys.* **48** (1968) 4517

³Brown and Sears, *J. Mol. Spectrosc.* **75** (1979) 111

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PRECISION SPECTROSCOPY FOR MEDICINE: PERSPECTIVES OF INTEGRATING BREATH-RELEVANT MOLECULES INTO HITRAN

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The 2024 edition of the HITRAN database includes spectroscopic parameters and absorption cross sections for numerous molecules which are used for modeling planetary atmospheres [1]. Yet HITRAN's utility extends beyond atmospheric and astronomical applications, the HITRAN database can play a critical role in advancing global public health through breath-based disease diagnostics. Respiratory diseases remain a leading cause of mortality worldwide, with Chronic Obstructive Pulmonary Disease ranking among the top three causes of death globally [2]. Non-invasive breath analysis offers a promising avenue for early detection and monitoring of such conditions, yet this potential is constrained by gaps in available spectroscopic reference data. The objectives of this work are threefold: to catalog necessary biomarkers, evaluate their representation in HITRAN and the broader literature regarding public accessibility, and establish a set of priorities for the spectroscopic community. Notable examples of gas-phase molecular spectra essential to medical diagnostics but absent or with limited spectral coverage within current literature include; methyl nitrate, pentamethylheptane, acetone and ethane. While these compounds serve as biomarkers for conditions ranging from oxidative stress and Type 1 diabetes to lung cancer and airway inflammation [3, 4] they are frequently unrepresented in reference databases. In their absence, researchers often default to gas chromatography-mass spectrometry (GC-MS), yet this approach faces challenges: non-polar hydrocarbons often elute simultaneously and cannot be distinguished, whereas polar aldehydes stick to the column matrix, necessitating a chemical conversion via Brady's reagent (DNPH) to form separable hydrazones prior to detection [5-8]. Expanding HITRAN to incorporate these biomarkers would significantly enhance its medical relevance and enable global communities to access efficient, direct gas-phase detection through reliable reference data in a standardized format.

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EXPLORING THE CHIRALITY OF FLEXIBLE MOLECULES USING ROTATIONAL SPECTROSCOPY

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High-resolution microwave spectroscopy has emerged as a powerful and versatile tool for the investigation of chiral molecules in the gas phase. When combined with phase-sensitive methods such as microwave three-wave mixing, microwave spectroscopy allows for sensitive chiral recognition and enantiomer-specific measurements. Beyond characterization, tailored microwave fields can be used to manipulate molecular populations and coherences in selected rotational states, opening pathways toward the quantum control of chiral molecules and the exploration of fundamental chiral dynamics. This is particularly interesting for structurally flexible chiral molecules that undergo tunneling.

The quantum dynamics of molecular states in double-well potentials provides a fundamental framework for understanding quantum tunneling, state localization, and symmetry breaking in molecular systems, chemical reaction processes, and related quantum phenomena. These dynamics are governed by the coupling between wavefunctions localized in the two wells, which are therefore highly sensitive to the details of the potential profile, including barrier height, well width, and potential symmetry.

To investigate this, we systematically studied benzyl alcohol and its D- and ¹³C-substituted isotopologues using high-resolution rotational spectroscopy. While the parent species undergoes typical symmetric chiral tunneling, mono-substitutions outside the symmetry plane break the potential symmetry through subtle difference in zero-point vibrational effects, leading to intriguing partial localization of tunneling states that is characterized in the rotational spectra.

Together with an overview of recent spectroscopic results for chiral molecular systems, this contribution will also highlight how subtle perturbations can affect quantum tunneling dynamics, providing fundamental insights into inter-well coupling in asymmetric double-well potentials.

GROUND-STATE ENERGY LEVELS OF METHANE WITH kHz-LEVEL ACCURACY FROM COMB-REFERENCED DOUBLE-RESONANCE AND LAMB-DIP SPECTROSCOPIES

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Methane is an extensively studied spherical top molecule, but its ground-state (GS) rovibrational energy levels are not yet known with state-of-the-art kHz-level precision because restrictive selection rules prevent transitions between states of different symmetry and parity [1]. We report the measurement of GS combination differences (CD) with kHz-level accuracy using two frequency-comb-referenced sub-Doppler techniques: optical-optical double-resonance (OODR) spectroscopy in the Λ -type configuration, and Lamb-dip spectroscopy (LDS) of allowed and forbidden ν_3 band transitions [2].

In Λ -type OODR (Figure 1a), a cavity-enhanced $1.67\ \mu\text{m}$ continuous-wave (CW) laser drives a $2\nu_3$ transition (ν_{ad}) [3,4], and a single-pass $3.3\ \mu\text{m}$ CW laser induces a $2\nu_3 \rightarrow \nu_3$ transition (ν_{dc}). Figure 1b) shows the OODR spectrum of the $2\nu_3$ R(0, A_1) transition when the $3.3\ \mu\text{m}$ laser is detuned by 4 MHz from the P(2, A_1) $2\nu_3 \rightarrow \nu_3$ transition. The separation of the two peaks, corresponding to the two lasers co- and counter-propagating with respect to each other, allows accurate determination of the $2\nu_3 \rightarrow \nu_3$ transition frequency. Combined with previously measured ν_3 fundamental band transition frequencies (ν_{bc}) [5,6], OODR measurements determine CDs between GS levels ($\delta\nu_{GS}$) of opposite parity and rotational quantum numbers J differing by up to 3. Using LDS, we measure CDs between levels of the same parity and $\Delta J \leq 2$. We fit a Hamiltonian model to 60 new $\delta\nu_{GS}$ values from LDS, 13 from OODR, and 49 from previous infrared, microwave and RF measurements, and obtain GS energies for levels with $J \leq 12$ with kHz-level accuracy, which is orders of magnitude better than available in databases HITRAN and ExoMol [1]. These GS term values set a new benchmark for spectroscopic characterization of methane.

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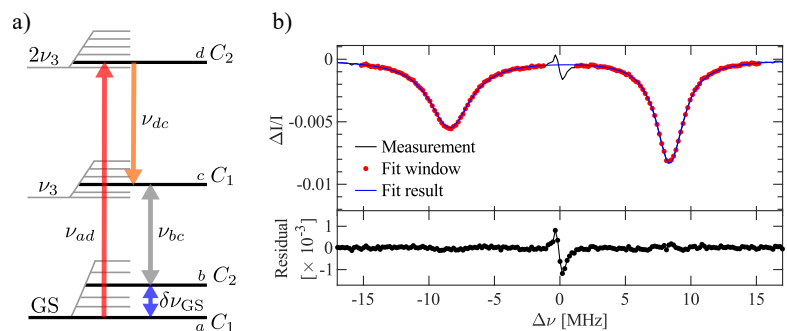


Figure 14: a) Schematics of the rovibrational energy levels addressed by Λ -type OODR. $C_{1,2}$ indicates the symmetry, in the Λ -type configuration, and C , and parity 1,2, of the levels. b) OODR spectrum of the $2\nu_3$ R(0, A_1) transition.

OPTICAL FREQUENCY COMB FOURIER TRANSFORM SPECTROSCOPY OF DIBROMOMETHANE IN THE 8 μm REGION

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Dibromomethane (CH_2Br_2) is a marine-emitted halogenated volatile organic compound that plays a role in atmospheric bromine chemistry and ozone depletion. Its spectroscopic detection is therefore important for both environmental monitoring and assessing potential anthropogenic contributions, such as disinfection by-products from ballast water treatment.

To support the development of CH_2Br_2 spectroscopic detection, we recorded its high-resolution absorption cross-section in the 1180–1220 cm^{-1} region (Figure 1) using optical frequency comb Fourier transform spectroscopy (FTS). Although it is not currently represented in databases like HITRAN [1], this spectral region, dominated by the strong CH_2 wagging (ν_8) mode, is suitable for sensitive detection of CH_2Br_2 .

The reported cross-section [2] shows good agreement with the PNNL database [3], while resolving spectral features in much greater detail (see inset). The rovibrational structures of the $\text{CH}_2^{79}\text{Br}^{81}\text{Br}$, $\text{CH}_2^{79}\text{Br}_2$, and $\text{CH}_2^{81}\text{Br}_2$ isotopologues were resolved and investigated using both an empirical fit implemented in PGOPHER [4] and an effective Hamiltonian framework [5].

The empirical treatment yields accurate band parameters, reproducing the measured spectra with an RMS residual of 0.00037 cm^{-1} . This represents a clear improvement over previously reported narrow-band studies [6], providing more consistent agreement across the observed spectral region. The effective Hamiltonian model captures polyad interactions and yields the first *ab initio*-based calculated line intensities in the 8 μm region.

Together, the cross-section and spectroscopic models provide a robust foundation for atmospheric detection of dibromomethane.

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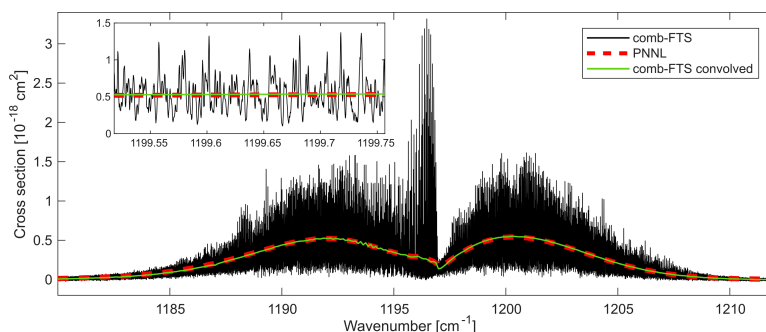


Figure 15: Absorption cross-section of CH_2Br_2 measured at 31 μbar using comb-based FTS (black) compared to the PNNL data [2] (red dashed). The solid green trace shows the cross-section from this work convolved with a *sinc* function to mimic the resolution of PNNL spectra. The inset shows a zoom around 1199.65 cm^{-1} .

TENTATIVE DETECTION OF SD^+ IN THE ORION BAR

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The isotopic ratio of a molecule provides information about its chemical evolution in space. The hydrogen isotopic ratio in space is $\text{D}/\text{H} \sim 10^{-5}$, but this ratio is one order of magnitude higher in Earth oceans. This results from deuterium enrichment by exothermic reactions starting with $\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$ in low-temperature interstellar clouds. Hence, tracing an isotopic ratio of hydrogen in a molecule allows us to solve chemical evolution in space. Especially, a ratio of a protonated atom to its deuterated species can trace the initial phase of chemical evolution due to the contribution of the reaction pair of $\text{H}_3^+ + \text{X} \rightarrow \text{XH}^+ + \text{H}_2$ and $\text{H}_2\text{D}^+ + \text{X} \rightarrow \text{XD}^+ + \text{H}_2$, where X is the atom. A deuterated ratio of a protonated atom, XD^+/XH^+ , is crucial information to constrain astrochemical models, because the ratio of the first deuterated species in space, i.e., $\text{H}_2\text{D}^+/\text{H}_3^+$, can be unveiled using this ratio. However, XD^+/XH^+ is difficult to measure.

CH^+ , OH^+ , SH^+ , CIH^+ , HeH^+ , and ArH^+ were detected in space, and for CH^+ , the deuterated species, CD^+ , were observed in the same cloud as SH^+ [A&A 651, A9, 2021]. However, the complex profile of CD^+ does not allow for the derivation of CD^+/CH^+ . Hence, at present, no reliable XD^+/XH^+ ratio for a protonated atom has yet been determined observationally.

The line of SD^+ was tentatively detected with an $\text{S/N} = 2.4$ for the $N_J = 1_2\text{--}0_1$ transition at 271.406 GHz toward the Orion Bar using the IRAM 30m telescope [Res. Notes AAS 10, 113, 2026]. This line shows $T_{\text{mb}} = 11 \pm 4$ mK with a width of 1.8 ± 0.7 km/s at the same velocity as the clear detection of another sulfur-bearing cation, HCS^+ . Based on the reported SH^+ column density [A&A 569, L5, 2014], this suggests a deuteration ratio of the protonated atom, SD^+/SH^+ , as 0.4 – 0.5 %, which is clearly lower than the DCN/HCN ratio of 1.1% in the nearby clump [A&A 508, 737, 2009]. Although the deuteration ratio for SH^+ is lower than that of HCN , they are broadly compatible.

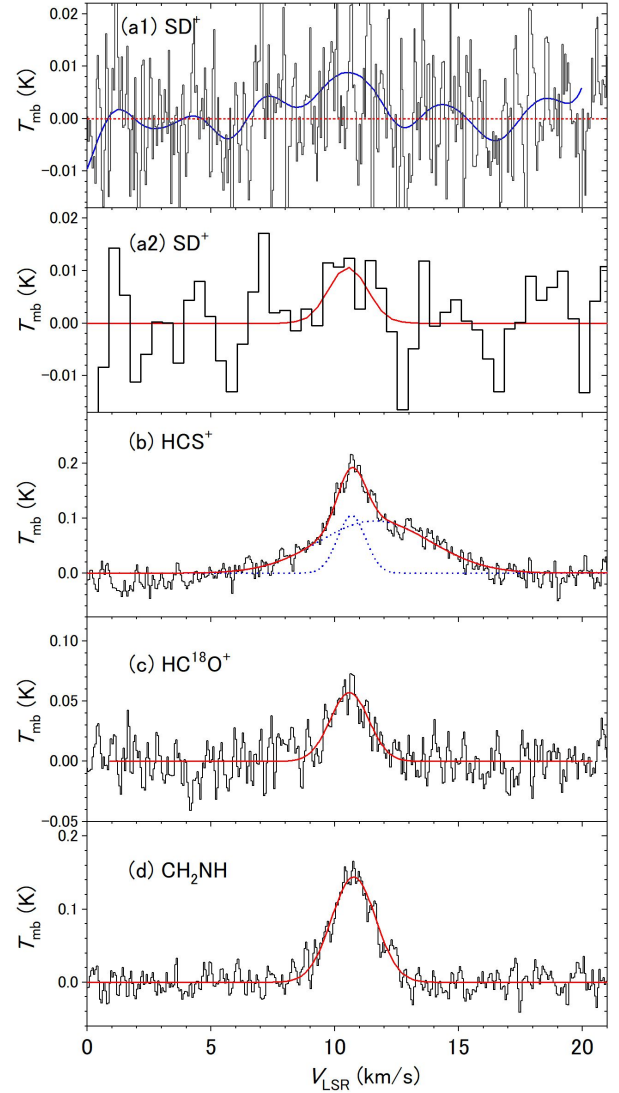


Figure 16: Observed lines in the Orion Bar using the IRAM 30m telescope. (a1) The tentatively detected $N_J = 1_2\text{--}0_1$ line for SD^+ . The blue line is the convolution of the spectrum with a Gaussian having an FWHM of 1.8 km/s. (a2) The black spectrum is obtained by averaging each 400 kHz block of the (a1) spectrum, and the red line is the result of a Gaussian fit. (b) The $J = 6 - 5$ line at 256.027 GHz for HCS^+ . (c) The $J = 3 - 2$ line at 255.479 GHz for HC^{18}O^+ . (d) $J_{K_a,K_c} = 4_{0,4}\text{--}3_{0,3}$ for CH_2NH at 254.685 GHz.

BRIDGING THE METROLOGICAL GAP BETWEEN SPECTROSCOPIC LINE PARAMETERS AND SPECIES CONCENTRATIONS RETRIEVED BY GAS ANALYZERS.

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Gas analyzers based on spectroscopic techniques such as optical-feedback cavity-enhanced absorption spectroscopy (OFCEAS) cavity ringdown spectroscopy (CRDS) and tunable diode laser absorption spectroscopy (TDLAS) have become powerful tools for sensitive and selective trace-gas quantification in process monitoring, emissions control, and gas-purity assessment. Their quantitative output, however, rests entirely on the accuracy of spectroscopic line parameters - line intensities, pressure-broadening and pressure-shift coefficients - that underpin the absorption models used to derive amount-of-substance fractions (concentrations) from measured spectra. Where database values (e.g. HITRAN) are not traceable to the international system of units (SI) and carry uncertainties exceeding the target measurement uncertainty, the metrological data quality of the analyzer's results is correspondingly limited, and the SI traceability of the reported result is broken. This contribution illustrates how the two complementary activities of PTB, i.e. the determination of the traceable absorption line parameters and the operation of laser spectrometers for amount-of-substance measurements - can be coupled to close this gap. Using high-resolution Fourier-transform spectroscopy (Bruker IFS 125HR) together with well-known gas samples, we metrologically determine and validate line intensities and broadening coefficients for relevant species such as H₂O, NH₃, and CO under exceptionally controlled conditions. We then show how feeding these newly measured line parameters improves the accuracy and traceability of laser spectroscopic amount fraction results. Thus, this work showcases the direct link between high-resolution laboratory spectroscopy and applied gas analysis, demonstrating that metrological-grade line data are an indispensable foundation for reliable instrument performance (either own development or commercial laser spectrometer).

JET-COOLED ROTATIONAL SPECTROSCOPY OF ETHYL LACTATE: CONFORMATIONAL LANDSCAPES AND CONVERSIONS

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Broadband rotational spectroscopy provides a powerful approach for resolving the conformational landscapes of flexible molecules with high structural precision. In this study, the rotational spectrum of ethyl lactate ($\text{C}_5\text{H}_{10}\text{O}_3$) was recorded using a broadband chirped pulse-Fourier transform microwave (CP-FTMW) spectrometer in the 2–6 GHz frequency range¹. Ethyl lactate is a chiral ester containing one stereogenic carbon atom. It comprises several functional groups, including the highly polar hydroxyl and ester groups and the nonpolar methyl and ethyl groups, creating a molecule with distinctive chemical and physical properties. CREST², a recently developed conformational searching tool, was used to generate possible low-energy structural candidates, which were subsequently subjected to geometry optimization and harmonic frequency calculations at the B3LYP-D3(BJ)³/def2-TZVP level of theory. Three conformers were unambiguously identified in the observed spectrum, which are the most stable among a list of ten distinct conformers predicted within an energy window of 10 kJ mol⁻¹. To further explore the energy ordering of the observed conformers and conformational conversion paths, we compared the relative intensity variations using three different carrier gases, i.e., helium, neon, and argon. In addition, extensive ¹³C and ¹⁸O isotopologue assignments for the three observed conformers provided the experimental basis for determining the substitution (r_s), effective (r_0), and semi-experimental equilibrium (r_e^{SE})⁴ molecular structures. To gain further insight into the conformational landscape, one-dimensional potential energy surface scans were carried out to map the torsional motions that interconvert the low-energy conformers. In addition, noncovalent interaction (NCI) analyses⁵ were performed to identify and visualize the weak intramolecular interactions that contribute to conformational stability. The combined experimental and computational results provide a comprehensive characterization of the conformational landscape and molecular structures of ethyl lactate, demonstrating the effectiveness of broadband rotational spectroscopy for investigating flexible chiral molecules.

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GENERAL FITTING CODE: MAIN FEATURES AND APPLICATIONS

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Current spectroscopic analysis programs have enabled the study of a wide range of molecular systems. As these systems become increasingly complex, however, existing software packages often encounter practical and methodological limitations. The primary objective of General Fit Code (GFC) is to provide a unified graphical environment capable of performing the entire workflow of high-resolution molecular spectroscopy, from spectral analysis and line assignment to Hamiltonian construction, spectral prediction, and least-squares fitting. The ultimate goal is to support all physical effects currently available in established programs such as SPFIT/SPCAT¹, PGOPHER², and XIAM³ among others, while also providing the flexibility required to go beyond these existing capabilities.

This is achieved through a highly general approach in which the molecular Hamiltonian is defined through arbitrary matrix elements rather than a fixed set of predefined models. Consequently, rotational, rovibrational, torsional, and hyperfine effects can be treated within a common formalism.

This contribution demonstrates the capabilities of GFC through several practical applications, ranging from conventional rotational analyses to systems involving internal rotation, rovibrational perturbations, multiple interacting vibrational states, and nuclear quadrupole hyperfine structure. Particular attention is devoted to matrix-Hamiltonian construction, eigenstate classification, and quantum-number assignment in the presence of strong resonances and state mixing.

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LABORATORY MILLIMETER- AND SUBMILLIMETER-WAVE SPECTROSCOPY OF THIOACETONE, FROM 150 TO 500 GHz FOR HOT-CORE SEARCHES

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Sulfur chemistry in the interstellar medium remains a key issue for understanding sulfur depletion, shock chemistry, and the molecular inventory of star-forming regions. In this context, thioacetone, $(\text{CH}_3)_2\text{CS}$, the sulfur analogue of acetone, $(\text{CH}_3)_2\text{CO}$, is a relevant target for astrochemical searches, following previous laboratory and astronomical work on related molecules¹. The molecule contains two equivalent threefold methyl internal rotors, which produce a complex rotational spectrum affected by torsional tunneling and internal-rotation splittings. However, previous laboratory data for thioacetone² were limited to the centimeter-wave region, with the microwave study reaching 36 GHz. Low frequency data are insufficient for reliable predictions in the millimeter and submillimeter domains. We report a laboratory study of the rotational spectrum of thioacetone, $(\text{CH}_3)_2\text{CS}$, recorded between 150 and 500 GHz with the FLASH spectrometer³ at the University of Lille. The internal-rotation structure was analyzed using ERHAM⁴. The resulting catalog was used for a first astronomical search.

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²Kroto et al., Chemical Physics Letters, 1974

³Motiyenko et al., Review of Scientific Instruments, 2020.

⁴Groner, The Journal of Chemical Physics, 1997

QUANTUM CHEMISTRY CALCULATIONS OF EXCITED STATES OF CHIRAL DIMERS : A FIRST STEP TOWARDS TIME-RESOLVED CHIRAL RECOGNITION

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Molecular chirality is ubiquitous in living organisms and most biochemical processes involve chiral interactions which are strongly enantio-sensitive : they basically depend on the enantiomeric form of the interacting partners. The ability of a chiral probe to distinguish the enantiomeric nature of a target, which is known as chiral recognition, plays a crucial role in many fields including biochemistry, pharmacology and drug design. Therefore, a great deal of attention has been devoted to the recognition process during the past decades but its underlying mechanisms remain elusive.

Previous studies have mainly focused on the characterization of the electronic and nuclear static properties of chiral complexes. Experiments and calculations have been employed to shed light on the outputs of homo- and hetero-chiral complexation in terms of e.g. binding and chirodiastaltic energies, harmonic frequency shifts relative to molecular components and dichroic properties such as circular dichroism and optical rotation [1-3]. However, the dynamics of clustering is still unknown.

Our objective is to picture the dynamics of chiral recognition by studying its reverse process. In practice, we aim at inducing the dissociation of an electronically excited chiral dimer, using a short pump laser pulse in the UV range, and probe the chiral dynamics using a delayed ionizing pulse in the femtosecond timescale. Time-dependent chirality will be rationalized using photoelectron circular dichroism, in the spirit of the work [4] performed for isolated methyl-lactate molecules.

A theoretical description of this pump-probe scenario needs for an accurate description of the excited states of the chiral dimers, populated by the pump. Up to our knowledge, it does not exist any previous study on low- and high-lying excited states of chiral dimers. Our work is directed at remedying this. In practice, we will present at the Conference our work on dimers of propylene oxyde, focusing on the description of excited states by means of time-dependent density functional theory (TDDFT) and multi-configurational second order perturbation theory (CASPT2). The results of the two approaches will be compared, considering various underlying Gaussian basis and functionals in the TDDFT framework as well as active spaces of increasing size in the CASPT2 method. Special attention will be paid to the characterization of the excited states and to the identification of dimer vibrational modes and frequency shifts. An illustration of TDDFT/CASPT2 comparison is given in Figure 1.

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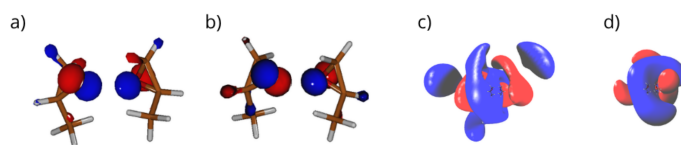


Figure 17: Molecular orbital isosurfaces of the highest occupied molecular orbital (HOMO, (a)) and HOMO-1 orbital (b) of the most stable dimer of propylene oxyde, obtained by means of TDDFT using a double zeta + double Rydberg Dunning-Hay underlying Gaussian basis and LCBLYP functional. Isosurfaces of the outer electron wavefunction relative to the first excited state issued from the same TDDFT calculations (c) and CAS(4,26)-PT2 (d) calculations.

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STEPWISE HYDRATION SWITCHES ELECTRONIC STRUCTURE IN A BIFUNCTIONAL ORGANOCATALYST THROUGH DOUBLE HYDROGEN BONDING

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1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) is a widely used bifunctional organocatalyst; however, its microscopic behavior in hydrogen-bonding environments remains poorly understood. In this study, we employed broadband rotational spectroscopy to identify the stepwise microhydration of TBD with one to four H₂O molecules and investigated how solvent molecules progressively alter its structure and electronic properties. We found that the bifunctional character and rigid bicyclic skeleton of TBD govern the growth of the hydrogen-bond network, while simultaneously inducing significant geometric distortion in the TBD skeleton. Notably, the formation of double hydrogen bonds induces pronounced ring twisting and drives an electronic structural transition from a ‘ π -localized” to a ‘ π -delocalized” state (shown in **Figure 1**). The water-induced electronic structure rearrangement is supported by experimental nuclear quadrupole coupling constants and theoretical natural population analysis. These results demonstrate that the basicity and reactivity of TBD are not inherent constants but can be dynamically modulated by local hydrogen-bonding networks, offering new insights into the design of more efficient hydrogen-bond-assisted catalytic systems.

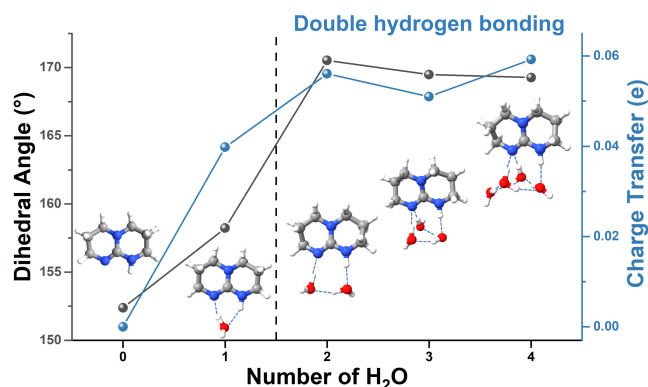


Figure 18: The microhydration process of TBD reveals that the dihydrate, stabilized by double hydrogen bonds, represents a critical turning point.

HIGH-ACCURACY SPECTROSCOPY OF THE OXYGEN B BAND FOR ATMOSPHERIC REMOTE SENSING AND HITRAN2024

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Molecular oxygen is a key reference species in atmospheric spectroscopy because its amount fraction is nearly constant throughout the Earth's atmosphere. Consequently, accurate spectroscopic parameters of O₂ transitions are essential for retrieving pressure and temperature profiles, determining total air column density, and improving the precision of greenhouse gas and air pollutant retrievals from satellite and ground-based observations.

The O₂ B band ($b^1\Sigma_g^+(v=1) \leftarrow X^3\Sigma_g^-(v=0)$), centered near 690 nm, is the second strongest atmospheric absorption band of oxygen. Although significantly weaker than the A band, its lower intensity reduces saturation effects over long atmospheric paths, making it particularly well suited for space-borne remote sensing. The B band is currently exploited by instruments including EPIC on the DISCOVER mission and the Sentinel-5 and Sentinel-5P missions.

Recent high-resolution, high signal-to-noise laboratory measurements have enabled a comprehensive characterization of air-broadened line shapes in the O₂ B band [1] using the speed-dependent Nelkin–Ghatak profile [2,3,4]. This analysis provided, for the first time, consistent beyond-Voigt line-shape parameters together with their temperature dependences for representative transitions across the band. Based on these measurements, we established empirical parameterizations describing the rotational dependence of the line-shape parameters [5]. Several parameters exhibit distinct trends for the P and R branches and, in some cases, for individual sub-branches. The derived parameterization allows the measured dataset to be extended to higher rotational quantum numbers by using trends established for the O₂ A band.

The resulting spectroscopic model provides a consistent description of air-broadened O₂ B-band spectra over atmospheric conditions. These parameters have been incorporated into the HITRAN2024 database [6] and are expected to improve forward radiative-transfer calculations and retrieval algorithms that rely on oxygen absorption as an atmospheric reference.

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HIGH-ACCURACY HD LINE-SHAPE ANALYSIS WITH HETERODYNE CAVITY RINGDOWN SPECTROSCOPY

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Molecular hydrogen (H_2) and its isotopologues have recently emerged as powerful platforms for probing new physics beyond the Standard Model, testing models of molecular collisions, determining the proton-electron mass ratios, investigating potential fifth forces, and validating relativistic and quantum-electrodynamical theories. Accurate hydrogen line intensities, line positions, and collision-induced line-shape parameters under varying thermodynamic conditions are also crucial in astrophysics for modelling of atmosphere of exoplanets and stars.

Reaching high experimental accuracy is a challenge in line-shape studies. Commonly used cavity ring-down spectroscopy (CRDS) provides ultra-high precision ($< 0.01\%$) but its accuracy is typically limited to several percent due to inaccuracies in light intensity measurements [1, 2, 3]. To overcome this limitation, we developed a heterodyne cavity ringdown spectroscopy (HCRDS) method [3]. This approach exploits the optical frequency information contained in the cavity's electromagnetic field by heterodyne detection of the ringdown signals, followed by Fourier analysis. It achieves sub-per-mil accuracy, which has been validated against *ab initio* CO line intensities.

We investigated the HD P(3) 2–0 transition using HCRDS and performed a multi-spectrum analysis of the absorption and dispersion spectra with several collisional line-shape models. Generally, the speed-dependent hard collision profile (SDHCP) or the more advanced β -corrected SDHCP (β -SDHCP) [4] are commonly used to analyze molecular hydrogen spectra at low pressures, while speed-dependent billiard-ball profile (SDBBP) [5] is considered at intermediate pressures (around atmospheric conditions). However, our results show that even at very low hydrogen pressures (up to 0.05 atm), SDBBP performs better than β -SDHCP and going beyond the β -SDHCP provides higher-accuracy of the line intensity. Fixing of one of the line-shape parameters affecting the width of a collision-broadened spectral line to *ab initio* value is enough to show that β -SDHCP results deteriorate significantly, while SDBBP provides stable, high-quality fits. Note that, fixing one of these parameters is a common approach to remove the numerical correlations between them which are relatively strong for weak hydrogen lines at low and moderate pressures. In addition to achieving permille level agreement with *ab initio* line intensities, SDBBP independently confirms the HD line position determined by vibrational saturation spectroscopy [6]. Despite low pressures and the resulting partial correlations between line position and shift, fixing the position to the value reported in Ref. [6] does not degrade the SDBBP fit quality.

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SUB-DOPPLER SPECTROSCOPY OF METHANE IN THE THz RANGE

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Methane plays a crucial role in atmospheric and planetary sciences, as one of the primary anthropogenic greenhouse gases. Its accurate spectroscopic characterization is essential for climate modeling and improvement of databases. Over the past decades, extensive spectroscopic studies have been carried out in the mid-infrared and visible regions, providing large datasets of transition frequencies, intensities and pressure broadening coefficients. However, in the THz domain, experimental data remain deficient and no sub-Doppler measurements have been reported in the THz range so far. This lack of high-precision data limits the refinement of spectroscopic model and datasets. Methane as a spherical top molecule, has no permanent dipole moment. As a result, pure rotational transitions are electric-dipole forbidden, making conventional microwave and terahertz spectroscopy very challenging. However, weak transitions can arise through different mechanism that induce a dipole moment. Such mechanisms are centrifugal distortion and vibration-rotation interaction. These effects relax the strict selection rules and enable otherwise forbidden transition to be observed. In the 100-1000 GHz range, the most intense transitions observed at the room temperature are pure rotational transitions in the ν_4 vibrational mode. In this work, we present sub-Doppler double-resonance (DR) measurements of methane in the ν_4 vibrational band allowing for first Sub-Doppler measurements of these lines. Our DR scheme, exploit a MIR pump radiation that selectively pump molecules into ν_4 state while THz radiation probe pure rotational transitions in this state. Resolving pure rotational transitions in 300-1100 GHz in the sub-Doppler regime enables improvement of frequency accuracy for refining effective Hamiltonian models and spectroscopic databases.

FIRST SPECTROSCOPIC STUDY OF A NEW INTERSTELLAR TARGET: ACETADIMINE ($\text{HN}=\text{C}(\text{Me})\text{NH}_2$)

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Most of the functions of organic chemistry are represented among the approximately 350 molecules detected to date in the interstellar and circumstellar medium, at least by the simplest compound. Exceptions include compounds such as those containing a nitroso CH_3NO ¹, and nitro CH_3NO_2 group². However, in some cases, the lack of rotational spectroscopy prevents the detection of such compounds. This is the case for amidines, compounds possessing a $\text{C}(=\text{NH})\text{NH}_2$ group. We began the study of these compounds with the methylated derivative, acetamidine $\text{HN}=\text{C}(\text{Me})\text{NH}_2$, a moderately kinetically stable compound, with the aim of soon moving on to the highly reactive formamidine $\text{HN}=\text{CHNH}_2$. We measured and analyzed the spectra of acetadimine, a non commercial sample, up to 500 GHz with the FLASH (Fast Lille Absorption emission High resolution) spectrometer in Lille. It should be noted the treatment of the data is not obvious due to the internal rotation of the methyl group. The first spectroscopic results will be presented.

¹L. Margules et al, 2025, *ApJ* **986**, 136

²V. Illyushin et al, 2025, *J. Mol. Spectrosc.* **345**, 64

RECENT DEVELOPMENTS OF THE LILLE ICE TERAHERTZ EXPERIMENT: IMPROVED SENSITIVITY AND APPLICATIONS TO PROCESSED ASTROPHYSICAL ICES

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Rotational spectroscopy provides unparalleled molecular selectivity for the identification of gas-phase species and is therefore a powerful tool for investigating the chemical complexity of molecules released from interstellar ice analogs. We present recent developments of the Lille Ice Terahertz Experiment (LITE), an experimental platform designed to investigate the thermal and photochemical desorption of astrophysical ice analogs. LITE combines ultra-high-vacuum ice processing with chirped-pulse Fourier transform (CP-FT) rotational spectroscopy in the millimeter- and submillimeter-wave (terahertz) region, enabling broadband and sensitive detection of desorbed species under astrophysically relevant conditions.

We report recent results on the thermal desorption of UV-irradiated methyl formate (HC(O)OCH_3) ices and introduce a new data-processing pipeline developed for temperature-programmed desorption (TPD) experiments. The new processing approach improves the sensitivity of the spectrometer. For light molecules such as water and methanol, the detection limit reaches number densities of approximately 10^9 cm^{-3} with integration times below 5 s. These improvements enhance the capability of LITE to detect low-abundance products formed during the processing of astrophysical ice analogs.

OBSERVATION AND DEPERTURBATION OF HIGHLY EXCITED STATES IN RbCs. EVIDENCE OF NON-ADIABATIC COUPLING

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Several new excited states in RbCs were observed by PLS in the region $20500 - 23700 \text{ cm}^{-1}$. Several thousand transitions to $4^1\Pi$, $5^1\Pi$ and $6^1\Sigma$ states were assigned. As expected, the rovibrational structure revealed numerous perturbations of different characters. Nevertheless, part of the experimental observations appears as regular and could be described by means of molecular constants and potential curves. Deperturbation analyses have been performed for the $4^1\Pi$ and $6^1\Sigma$ states. The existing theoretical calculations helped us to identify the main interacting states and to explain some of the strong perturbations through coupled channels models. However, the origin of part of the perturbations remains still unclear. The most striking examples can be found in the $6^1\Sigma$ state, where deviations up to several wavenumbers are observed. The rotational and spin-orbit interactions cannot explain them, because no electronic states of proper symmetry are situated nearby. The only possibility is to consider the non-adiabatic coupling [3] with the lower $5^1\Sigma$ state. Both adiabatic $^1\Sigma$ states according to the theoretical calculations, are result of several avoided crossings and the most prominent one is in the region where perturbations are observed. We will present the experimental data, the models used to describe them so far and we will discuss the future possible steps to reach full agreement between the theory and the experiment.

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ROTATIONAL SPECTROSCOPIC STUDIES OF AN ODOROUS CHIRAL TAUTOMERIC FURANONE: 4-HYDROXY-2,5-DIMETHYL-3(2H)-FURANONE AND ITS HYDRATES

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Chiral aroma compounds occurring in nature often display enantiomeric excess as a result of their stereoselective biogenesis, with their structure–odor relationships being influenced by non-covalent interactions [1]. Furthermore, since most aroma compounds are water-soluble, they can be easily influenced by water in the surroundings. First observed as a product of the well-known Maillard reaction [2], chiral 4-hydroxy-2,5-dimethyl-3(2H)-furanone (HDMF) is one of the most important aroma chemicals because of its low odor thresholds, easily detectable at low concentrations in air, and attractive burnt-sugar flavour properties [1]. As is shown in Figure 1, it features a unique keto-enol tautomerism leading

to its racemization, and its pleasant flavour is associated with a planar enol-oxo group of a cyclic dicarbonyl derivative [2]. Strong hydrogen bonding can be built due to the hydrophilic structure of HDMF [3]. This is of interest to investigate how water potentially influences this keto-enol racemization process through intermolecular hydrogen bonds. In our current studies, along with the conformer-rotamer ensemble sampling tool CREST [4], geometry optimizations at the B3LYP-D4/def2-QZVP level of theory were used to predict the structures of the HDMF monomer and hydrates, respectively. Rotational spectra of the HDMF monomer and its water complexes were recorded in both the 2–8 GHz and 8–12 GHz ranges by using the chirped-pulse Fourier transform microwave spectrometer COMPACT [5] and subsequently analyzed. Pure rotational transitions were assigned to the HDMF monomer and its hydrates HDMF-(H₂O)_{1–5}. The relationships between the geometries of the observed structures, the non-covalent interactions, and the tautomerism equilibrium of the HDMF-hydrates will be discussed.

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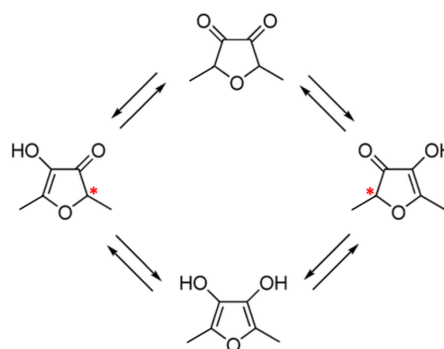


Figure 19: Keto-enol tautomerization of HDMF. The chiral centers are marked by red asterisks.

CASDA24: CALCULATED DATABASES FOR MOLECULAR SPECTROSCOPY

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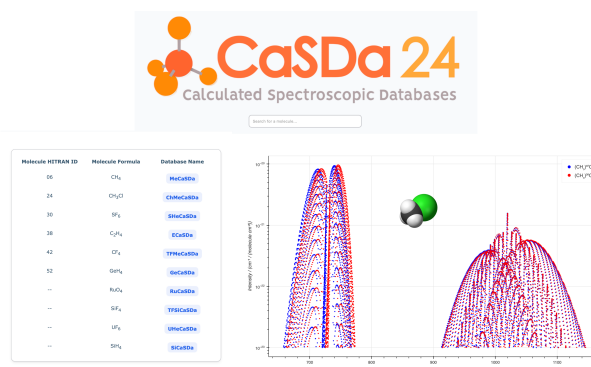
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We present CaSDa24¹², the latest version of our collection of high-resolution molecular spectroscopy databases. CaSDa24 currently consists of ten independent databases, each dedicated to a specific molecule (CH₄, CH₃Cl, SF₆, C₂H₄, CF₄, GeH₄, RuO₄, SiF₄, UF₆, SiH₄), and is set to evolve further. These databases include detailed lists of calculated spectral lines, eigenvectors, energy levels, and other relevant information derived from the latest analyses of experimental spectra.

This poster provides an overview of the current state of molecular spectroscopy databases, explains the fundamental principles of CaSDa24, and summarizes important updates and newly introduced data. In particular, we will demonstrate how this tool could be useful for the spectroscopy of exoplanet atmospheres.



¹C. Richard *et al.*, J. Quant. Spectrosc. Radiat. Transfer **327**, 109127 (2024).

²<https://vamdc.icb.cnrs.fr>

TOWARDS UNDERSTANDING LEAK-OUT SPECTROSCOPY (LOS) IN CRYOGENIC ION TRAPS

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Leak-Out spectroscopy (LOS) has proven to be a versatile tool in electronic, vibrational, ro-vibrational, and rotational spectroscopy of cold trapped ions¹²³⁴. The method relies on the transfer of internal to translational energy (V-T transfer) in collisions of the ions with neutral gas-phase atoms or molecules. Through the addition of kinetic energy, ΔE_{kin} , some ions overcome the static axial 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 $E_{kin} \approx kT_{ion}$ is the kinetic energy of the non-excited ions. As a result, it shall work best the larger ΔE_{kin} and the smaller E_{kin} while ΔE_{pot} shall be adjusted accordingly.

We report on systematic experimental investigations of the Leak-Out efficiency. Using CH_3^+ as a reference system, we compare different collision partners (He, Ne, Ar, N_2) as well as different vibrational modes (stretching vs. bending) using a semi-quantitative model of the Leak-Out process. The LOS efficiency is found to vary significantly between systems, and we discuss possible physical reasons. That could be, for instance, the polarizability of the collision partner and the nature of the excited vibrational mode. The purpose of this study is to better understand the factors that influence LOS efficiency on a quantitative level in order to establish systematic guidelines for the applicability of the method to new ionic systems.

¹P. Schmid et al., 2022, J. Phys. Chem. A, 126, 43

²M. Bast et al., 2023, J. Mol. Spectrosc., 398

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NEW EXPERIMENTAL SPECTRA AND QUANTITATIVE MODELING OF THE STRETCHING DYAD OF SILANE AND OVERTONES

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Silane (SiH₄) sits at the crossroads of two fields that rarely meet :

On one side, its stretching vibrations are being looked at as a way to separate the silicon isotopes ²⁸Si, ²⁹Si and ³⁰Si by infrared laser excitation, a route that matters more and more as isotopically pure ²⁸Si finds its way into quantum devices, better-behaved semiconductors (better q-bit coherence). On the other side, SiH₄ has actually been spotted out in space, in the dusty envelope of the carbon star CW-Leonis (IRC +10216), where we can only pin down how much of it is there if we know its line positions and intensities well.

This work continues our earlier study of the bending dyad ν_2/ν_4 ¹, moving up to the stretching region. We report new high-resolution Fourier-transform spectra of SiH₄ covering the stretching dyad ν_1/ν_3 ($\sim 2100\text{ cm}^{-1}$, 4.6μ) and, for the first time at this level of detail, the overtone and combination bands $2\nu_1$, $2\nu_3$ and $\nu_1+\nu_3$ ($\sim 4300\text{ cm}^{-1}$, 2.3μ) recorded at LISA . We treat the data with the tensorial formalism built for the T_d point group using an effective Hamiltonian and an effective dipole moment to model both positions and intensities.

The results will be included in the CaSDa database ².

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RO-VIBRATIONAL SPECTROSCOPY OF THE ALLENE CATION (C_3H_4^+)

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Ionisation of allene (D_{2d} symmetry) induces a Jahn–Teller distortion, leading to a D_2 symmetric cation, as has been evidenced with photoelectron spectroscopy and electron spin resonance spectroscopy.¹ The Jahn–Teller effect has fascinated molecular physicists for decades because of its complex impacts on molecular structure. One powerful strategy for investigating molecular structure is via precise measurements of their rotational constants. However, the only reported rotational constants of the allene cation do not definitively distinguish between D_2 and D_{2d} symmetry, because the rotational constants B and C were equal within uncertainties.

Here we report a leak-out spectroscopy (LOS)² study of the gas-phase allene cation. Two rovibrational bands (see Figure 1) were measured and rotationally analysed. These two bands allowed us to determine precise rotational constants and the resolved difference between B and C, unequivocally establishing D_2 symmetry for the allene cation in its ground states. Therefore, our results demonstrate that LOS can decisively determine the symmetry of a Jahn–Teller distorted cation, while also revealing unexpected spectral features that challenge current models.

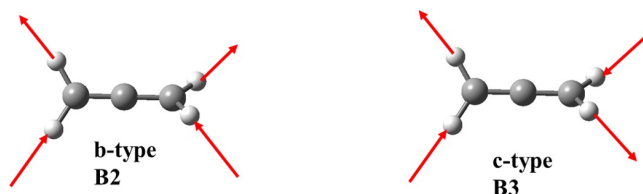


Figure 20: The two experimentally detected bands.

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HIGH-RESOLUTION LEAK OUT SPECTROSCOPY OF THE ETHYLENE CATION

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C_2H_4^+ has fascinated physical chemists for decades because it is a fundamental molecular ion with an ionisation from a double bond, which gives rise to a complicated potential energy surface (PES). Compared to the planar neutral ethylene, the C=C double bond of C_2H_4^+ slightly twists, and has a shallow double well PES, along which tunnelling is important. The description of this twisting is theoretically challenging,^{1,2,3,4} and so an experimental estimation of the equilibrium torsion angle would provide a valuable anchor.

We employ the Leak-Out Spectroscopy (LOS)⁵ to record high-resolution infrared spectra of the ethylene cation. C_2H_4^+ are stored in a cryogenic ion trap, with the trap barrier set such that the ions have barely not enough kinetic energy to exit the trap. The ions are then irradiated by an infrared laser to excite them rovibrationally. Excited ions can then collide with a neutral gas in the ion trap to transfer their vibrational energy into kinetic energy, allowing them to leak out of the trap and be detected. Using LOS, we measured two fundamental CH_2 stretching bands of C_2H_4^+ and one combination band, from which we determine the rotational constants of the ground and excited vibrational states, and ultimately estimate a semi-experimental torsion angle of ~ 20 degrees.

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HYPERFINE-RESOLVED VARIATIONAL NUCLEAR MOTION SPECTRA OF DIATOMIC MOLECULES

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Hyperfine structure arises from interactions of nuclear electric and magnetic multipole moments with the molecular environment, producing small splittings of rovibronic energy levels that are often difficult to resolve experimentally. Advances in high-resolution spectroscopy have made these splittings increasingly observable, creating a growing need for theoretical methods to accurately predict hyperfine-resolved spectra. There has been extensive theoretical work on hyperfine structure in diatomics, including theoretical derivations provided by Kato ^[1] and Brown and Carrington ^[2], as well as effective-Hamiltonian programs such as PGOPHER ^[3], where hyperfine interactions are added perturbatively to the rovibronic Hamiltonian because their splittings are much smaller than vibrational spacings. Based on the nuclear-motion program DUO ^[4], Qu *et al.* developed a fully variational method for diatomic molecules with only one non-zero nuclear spin ^[5], which was tested on MgH and NO and applied to the hyperfine-resolved spectroscopic model of VO ^[6].

In our recent work, this variational method was extended to homonuclear diatomic molecules containing two equivalent nuclei with non-zero spins ^[7]. The new implementation explicitly couples the two nuclear spins and accounts for the exchange symmetry of identical nuclei. Unlike conventional perturbative treatments, the variational treatment also allows hyperfine coupling between vibrational states to be included. It enables the calculation of hyperfine-resolved energy levels as well as electric-dipole and electric-quadrupole transition intensities. The method was tested on H₂, D₂, N₂, and its ion, including singlet, doublet, and triplet electronic states with $|\Lambda| = 0$ and 1, giving results in good agreement with available reference data from independent effective-Hamiltonian calculations. Future work will generalise the method to heteronuclear diatomic molecules containing two non-zero nuclear spins, such as HD and LiNa.

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THE ROTATIONAL SPECTRUM OF TRANS-2,3-EPOXYBUTANE: A COMBINED CHIRPED-PULSE FOURIER TRANSFORM AND ABSORPTION MICROWAVE STUDY

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Complex organic molecules are important for understanding the chemical evolution of the interstellar medium (ISM). Among the approximately 350 molecules listed in the Cologne Database for Molecular Spectroscopy,¹ as detected in the ISM or toward late-type stars, an increasing number belongs to cyclic species. Among them are several containing an O atom in the ring, for example the ubiquitous oxirane², which is also known as ethylene oxide, or its methyl derivative propylene oxide—the first chiral molecule detected in space.³ The molecule *trans*-2,3-epoxybutane can be viewed as the vicinal dimethyl-substituted derivative of oxirane and propylene oxide. Extending a previous microwave study,⁴ we recorded the rotational spectrum of *trans*-2,3-epoxybutane in the 12–375 GHz frequency range, utilizing a combined scheme of chirped-pulse Fourier transform microwave and frequency-modulated absorption spectroscopy. A group of *b*-type transitions with quantum numbers up to $J = 60$ and $K_a = 7$ have been assigned to the electronic and vibrational ground state. Owing to the internal rotation of the two equivalent methyl rotors, triplet-like patterns consisting of four components have been observed and assigned for many J values. The present work provides an accurate set of rotational and internal rotation parameters to facilitate the search for *trans*-2,3-epoxybutane across a wide range of physical conditions in the ISM, from cold molecular clouds to hot cores.

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EXOMOL LINE LIST FOR LOW-LYING ELECTRONIC BAND SYSTEMS OF $^{12}\text{C}^{16}\text{O}$

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A high-temperature line list is presented for the $^{12}\text{C}^{16}\text{O}$ $A^1\Pi-X^1\Sigma^+$ electronic band system, commonly known as the Fourth Positive system, the most extensively studied excited electronic system of carbon monoxide. A new high-accuracy spectroscopic model for the ground $X^1\Sigma^+$ and excited $A^1\Pi$ states has been developed¹ based on *ab initio* calculations performed at the aug-cc-pV5Z CASSCF/icMRCI+Q level of theory. The resulting potential energy curves and transition dipole moment functions were subsequently refined using the Duo program together with available MARVEL (Measured Active Rotational–Vibrational Energy Levels) empirical energy levels, significantly improving the accuracy of the final line list. Using the refined .states and .trans files, the comprehensive 4thplus line list includes both $A^1\Pi-X^1\Sigma^+$ electronic transitions and updated rovibrational transitions within the $X^1\Sigma^+$ ground state. Comparisons with several high-resolution experimental spectra show excellent agreement in both line positions and band structures, confirming the reliability of the present spectroscopic model.

In addition, theoretical investigations of nearby electronic states, including $I^1\Sigma^-$, $D^1\Delta$, $a'^3\Sigma^+$, $a^3\Pi$, $d^3\Delta$, and $e^3\Sigma^-$, are underway to extend the spectroscopic model. Current efforts focus on the $a^3\Pi$ state, which is expected to exhibit significant perturbations arising from interactions with neighbouring electronic states. A refined spectroscopic model for the low-lying vibrational levels of the $a^3\Pi$ state is presented and compared with available experimental energy levels, providing a foundation for the future development of a comprehensive coupled-state model for CO. This model will enable the generation of temperature-dependent line lists for the Cameron ($a^3\Pi-X^1\Sigma^+$) band system as well as transitions involving other nearby electronic states.

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REANALYSIS OF THE $B^2\Sigma^+ - X^2\Sigma^+$ SYSTEM OF $^{12}\text{C}^{17}\text{O}^+$ BY FT - UV EMISSION SPECTROSCOPY: $B^2\Sigma^+(\nu = 0, 1)$ LEVEL

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The carbon monoxide cation (CO^+), obtained from one of the most abundant molecules in the interstellar medium - CO - has been extensively studied for its dominant isotopologue. The $^{12}\text{C}^{16}\text{O}^+$ molecule has been identified both in the ISM through low-rotational transitions and in cometary spectra via the $A^2\Pi - X^2\Sigma^+$ transition [1]. In contrast, the $^{12}\text{C}^{17}\text{O}^+$ isotopologue has not yet been detected in astrophysical environments, despite the confirmed presence of $^{12}\text{C}^{17}\text{O}$ in the ISM, even given the low natural abundance of ^{17}O (0.04%).

In this work, we report high-resolution spectroscopic investigation of $^{12}\text{C}^{17}\text{O}^+$ carried out at the Materials Spectroscopy Laboratory, University of Rzeszów. The study focuses on the $B^2\Sigma^+ - X^2\Sigma^+$ electronic transition using Fourier-transform ultraviolet (FT - UV) emission spectroscopy. About 1000 ro-vibronic transitions of the 0-0, 1, 2, 3 and 1-0, 2, 3, 4, 5 bands, were measured with absolute uncertainties ranging from 0.0050 to 0.0100 cm^{-1} .

The analysis was performed using the PGOPHER software [2], enabling the determination of accurate molecular constants and energy level values for the $X^2\Sigma^+(\nu = 0 - 5)$ and $B^2\Sigma^+(\nu = 0, 1)$ states of the $^{12}\text{C}^{17}\text{O}^+$ isotopologue. The Dunham parameters (Y_{kl}) for the $X^2\Sigma^+$ state of $^{12}\text{C}^{17}\text{O}^+$ were determined.

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EXTENSION OF 2-ETHOXYETHANOL ROTATIONAL SPECTROSCOPY AND ITS SEARCH IN ISM

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Recent detections of chemically related alkoxy alcohols in the interstellar medium (ISM) ^{1,2,3} of 2-ethoxyethanol ($\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$) to facilitate its astronomical identification. Quantum-chemical calculations were first carried out to establish the relative stabilities of the molecular conformers and to predict their rotational spectroscopic properties. The rotational spectrum of the lowest-energy conformer, gg^+tt , was recorded with a combination of microwave and (sub)millimetre-wave spectrometers covering the frequency ranges 2–20 GHz, 6.5–18 GHz, 150–220 GHz, 230–330 GHz, and 370–500 GHz. Overall, 2628 rotational transitions were assigned and globally analyzed using a Watson A-reduced Hamiltonian, yielding precise rotational and centrifugal-distortion constants through the octic order. These spectroscopic parameters provide accurate frequency predictions for searches in astronomical spectra at (sub)millimetre wavelengths. The resulting line catalog was subsequently employed in a search for gg^+tt -2-ethoxyethanol toward NGC 6334I using ALMA observations. No spectral signatures of the molecule were identified.

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MODERN DFT SCALING FOR NUCLEAR QUADRUPOLE COUPLING CONSTANTS: QMBENCH.NET/NQCC/PARAMETRIZATION

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In high-resolution molecular spectroscopy, hyperfine splitting due to nuclear quadrupole coupling can be a double-edged sword. Depending on the magnitude of the observed splitting and the spectral resolution, it can greatly complicate spectral assignment. On the other hand, it contains useful information about the electronic environment surrounding a nucleus. To extract this information, the associated nuclear quadrupole coupling constants (NQCCs) must be determined from the experimental data. To do so, accurate predictions of these quantities preceding the experimental characterization is necessary.

Here, we present an interactive NQCC scaling approach that aims to significantly improve the agreement between theory and experiment by incorporating empirical results.

This procedure was first introduced by Bill Bailey.[1] The semi-empirical scaling yields an effective nuclear quadrupole moment, Q_{eff} , which can be used to enhance predictions. In the original approach, NQCCs were obtained from electric field gradient (EFG) calculations using experimentally determined monomer structures. Unlike the original formulation, we opted for a fully theoretical approach that does not require any *a priori* structure determination to simplify predictions. Each structure is optimized at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. Successive electric field gradient (EFG) calculations were performed at the B3LYP-D3(BJ,abc)/x2c-TZVPall level of theory with the relativistic exact two-component (X2C) theory implementation combined with the finite-nucleus model and relativistic picture-change effects, as well as without these corrections. Only systems are included for which the whole NQCC tensor was determined. Unlike Bailey's database, we now also include complexes in the training data. The website is fully interactive, and users can choose a subset of data using modifiers such as `\texttt{linear}`, `\texttt{complexes}`, `\texttt{radicals}`, *etc.*, and parameterize accordingly. Currently, only data for iodine is available. Here, the dataset comprises Bailey's original dataset combined with new data presented in our publication on fluorinated iodobenzenes.[2]

Don't like our choice of theory? The parametrization can be redone by any user, since we provide *.xyz* files for all structures and diagonalized experimental tensors for each reported nuclide with references. Simply download the dataset and run the calculations with your preferred method.[2,3]

Future updates to the website will expand the nuclei list to eventually encompass Bailey's website and beyond. To keep the dataset up to date with the literature, the website will eventually allow users to suggest publications to be added to the dataset.

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challenges for numerical quantum chemistry

HIGH RESOLUTION SPECTROSCOPY OF EXOPLANET BIOSIGNATURES WITH LARGE AMPLITUDE MOTIONS

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The search for extraterrestrial life drives exoplanet research, with over 7000 confirmed planets. The James Webb Space Telescope (JWST) and upcoming Ariel (Atmospheric Remote-Sensing Infrared Exoplanet Large-survey) missions stimulate detailed infrared studies of exoplanetary atmospheres. Several molecules, such as methanol and organosulfur species, have been proposed to be potential biosignatures in these atmospheres. Nevertheless, detecting these gases is challenging due to limited infrared data, especially for molecules with large amplitude motions containing one or two internal methyl rotor(s). New high-resolution data in the 600-1900 cm^{-1} spectral range for methanol and in the 600-1400 cm^{-1} range for dimethyl sulfide have been recorded at room temperature with Fourier Transform Infrared (FTIR) spectrometers located in Bruxelles and at the Synchrotron SOLEIL, respectively. These spectra are combined with rovibrational data recorded with the supersonic jet setup combined with a quantum cascade laser (QCL) source around 10 micron (SPIRALES) developed at MONARIS. New assignments extending previous results will be presented for both molecules^{1,2}. For methanol, the FTIR transmittance spectra were calibrated with OCS data from HITRAN³. A linelist with line frequencies and absorption cross-sections from the FTIR spectra was obtained using the WSpectra program⁴. Several new weak lines of methanol associated with $\nu_t = 2-0, 3-1, 3-0, 4-1$ bands were observed and analysed, using the global model of the BELGI programs⁵. For dimethyl sulfide more than 1900 new assignments in the ν_{14} band near the 10 micron region fit with a root-mean-square deviation of 0.0005 cm^{-1} close to measurement accuracy, and with values of the J quantum number up to 60, significantly extending the previous study which included 1119 lines up to $J=29$ only.⁶

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THE $^{13}\text{C}^{18}\text{O}$ $\text{A}^1\Pi(v=2) \sim \text{A}^3\Pi(v=13)$ INDIRECT PERTURBATION: DETECTION, MECHANISM AND SURPRISES

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A direct perturbation between the $\text{a}^3\Pi$ and $\text{A}^1\Pi$ vibrational levels of two electronic states that belong to the same electronic configuration of the carbon monoxide molecule should be unobservably weak because the vibrational overlap integral $\langle \text{a}^3\Pi, v' | \text{A}^1\Pi, v'' \rangle$ for their near degenerate levels is extremely small [1-4]. Yet level shift and transition intensity signatures of the $\text{a}^3\Pi(v=13) \sim \text{A}^1\Pi(v=2)$ perturbation are unmistakably present in the $^{13}\text{C}^{18}\text{O}$ isotopologue. Detailed study of the $\text{A}^1\Pi - \text{X}^1\Sigma^+(2, 0)$, $\text{B}^1\Sigma^+ - \text{A}^1\Pi(0, 2)$ and $\text{C}^1\Sigma^+ - \text{A}^1\Pi(0, 2)$ spectra, obtained on the VUV- and Vis-FT complementary techniques in the energy regions of the three crossing points (e- and f-symmetry, $|\Omega| = 0, 1, 2$) between the $\text{a}^3\Pi(v=13)$ and $\text{A}^1\Pi(v=2)$ states, reveal that the perturbation pathways are indirect, primarily facilitated by the $\text{e}^3\Sigma^-(v=4)$ state, and that quantum mechanical interferences between the F_{1e} and F_{3e} parts occur (Figure 1).

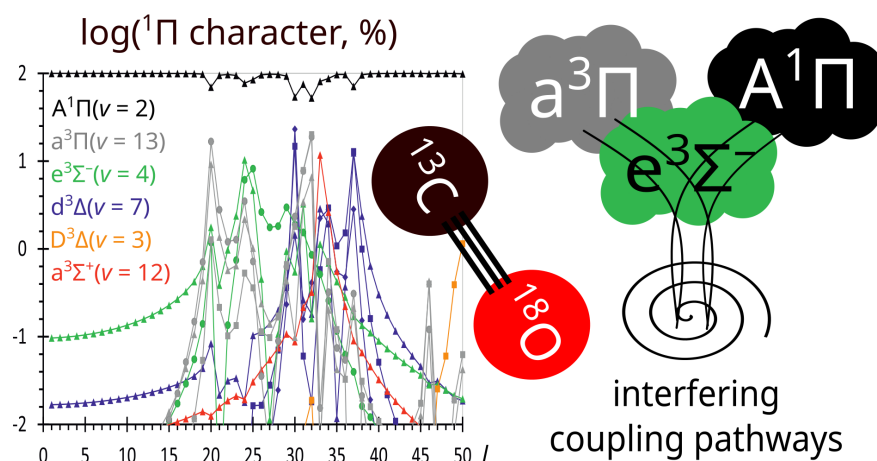


Figure 21: Graphical abstract

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HIGH-RESOLUTION SPECTROSCOPY OF HCOOCH_3 , SKELETAL TORSION

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⁵University of Saskatchewan, Canadian Light Source. Inc.

We have been studying the high-resolution spectroscopy of methyl formate (HCOOCH_3), with a particular interest in its vibrationally excited states. This molecule is one of the most abundant complex organic molecules in interstellar space. The pure rotational transitions in the first torsionally excited state, ν_{18} was reported in 2003¹, and those in the second torsional excited state have been identified in the laboratory and in space². The temperature in Orion KL is estimated to be as high as about 200 K. This prompts us to study low-lying vibrational states and with microwave and far-infrared spectroscopy.

In this paper, we report on the skeletal torsion excited state of methyl formate, ν_{17} . This state is located at about 332 cm^{-1} . The fundamental band was observed at Far-Infrared Beamline of the Canadian Light Source synchrotron. The resolution was instrument-limited to 0.00096 cm^{-1} . The ν_{17} spectrum is overlapped by the ν_{12} (C-O-C deformation) band at 312.3678 cm^{-1} ³. The P and R -branches of $K_c = 0 - 15$ of the A-species were assigned, using combination differences and cross correlation techniques. Figure 1 shows the part of the R -branch lines $K_c = 0, 1$ and $1, 2$ series. Limited number of transitions of the E-species were assigned. We are also working on the microwave data, and have some tentative assignments for the pure rotational transitions.

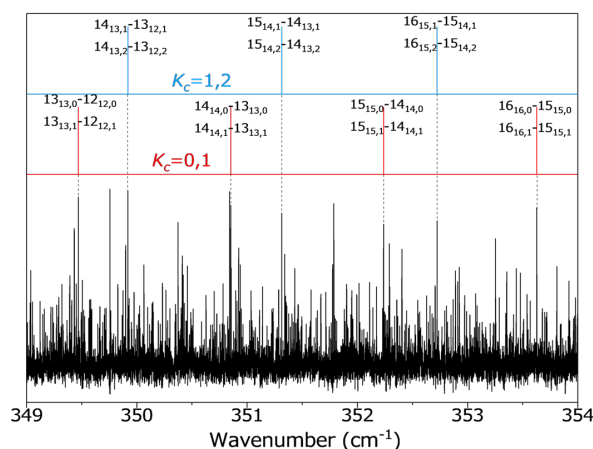


Figure 22: Part of the infrared spectrum with assigned R -branch lines $K_c = 0, 1$ and $1, 2$ series

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VACUUM COMPATIBLE PIEZO-ACTUATED MIRROR MOUNT WITH 80 KHZ BANDWIDTH

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³Namur Institute for Complex Systems, Université de Namur, Namur, Belgium

Optical cavities find many applications, in gravitational wave detection¹, nuclear fusion² and high-resolution molecular spectroscopy³. These applications rely on a coherence transfer between the laser and the cavity, effectively stabilising the cavity length using a high-bandwidth piezoelectric transducer (PZT)-actuated mirror. This coherence transfer then allows to compensate any length fluctuation in the cavity caused by environmental effects (vibrations from vacuum pumps, acoustic variations, etc). High-bandwidth PZT-actuated mirror mounts have been developed over the years, reaching bandwidths of several hundreds of kHz^{4,5}.

Because of the mechanical constraints and limited resonant frequency of a PZT, these mirror mounts need to be designed carefully.

Here we present a PZT-actuated mirror mount, whose design is based on Goldovsky's design⁴, in which the mirror is compressed with soft materials to damp mechanical vibrations between the mirror and the mount. Along with the mechanical design, the mount has been optimised so that all electronical components have the highest possible bandwidth. The PZT we use has a bandwidth of 260 kHz, and combined with our vacuum compatible mount, we have reached a bandwidth of 80 kHz. With the same design and improved electronics, we hope to reach a bandwidth higher than 100 kHz in the near future. This high-bandwidth PZT-actuated mirror mount will be used in our future prototype for the Einstein Telescope, ET-OPT.

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STUDY OF PREDISSOCIATIVE LIFETIMES OF CS^{2+} DICATION

Lukáš Hrubčík¹, Tereza Uhlíková¹

¹University of Chemistry and Technology Prague, Department of Analytical Chemistry

This work presents a spectroscopic model of the metastable carbon monosulfide dication (CS^{2+}) aimed at predicting its photoabsorption spectrum and assessing its detectability in astrophysical environments. High-level ab initio multireference configuration interaction (MRCI) calculations with state-averaged CASSCF reference wavefunctions were employed to compute potential energy curves, dipole moments, transition dipole moments, spin-orbit couplings, and electronic angular momenta for the five lowest-lying electronic states over extended internuclear distances. Rovibronic energy levels were calculated using the DUO program and bound and quasi-bound regions up to $25\,000\text{ cm}^{-1}$ were identified. Metastable states embedded within the Coulomb barrier were treated explicitly, with total resonance widths obtained by combining tunnelling, spin-orbit induced predissociation, and radiative decay utilizing stabilization diagrams methodology. These state-resolved energies and lifetimes were subsequently used to generate synthetic photoabsorption spectra and to quantify the relative contributions of predissociation and radiative broadening across the relevant bands. The resulting model provides predicted band positions, resonance widths, and lifetime trends for CS^{2+} , supplying reference spectroscopic data for future laboratory measurements and astrophysical modelling.

CROSS-ISOTOPOLOGUE VALIDATION OF A RESIDUAL LIGHTGBM MODEL FOR CO₂ ENERGY CALIBRATION

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¹Department of Physics, Khalifa University, P.O. Box 127788,

²Department of Artificial Intelligence, The University of Jordan, Queen Rania St, Amman, Jordan

³Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Rather than predicting absolute rovibrational energies, we formulate spectroscopic calibration as a residual-learning problem. For twelve stable CO₂ isotopologues, the physics-based baseline is defined as $\Delta E = E_{\text{MARVEL}} - \frac{1}{2}(E_{\text{Ames}} + E_{\text{CDSD}})$, and a LightGBM regressor learns the correction $\Delta E = E_{\text{MARVEL}} - E_{\text{mean}}$ from empirically derived MARVEL energies, Ames-2021, and CDSD-296 databases.

The model uses eight physically motivated inputs selected from more than forty candidates: the quantum-state descriptors (J, v_1, v_2, v_3, r, p) and the signed and absolute disagreement between the two calculated baselines. Shallow gradient-boosted trees are trained using a Huber objective with $\alpha = 0.90$, a learning rate of 0.01, row and feature subsampling, and early stopping to limit overfitting.

Transferability is evaluated using twelve-fold leave-one-isotopologue-out validation, in which every state belonging to the test isotopologue is excluded from training. Across 50,258 MARVEL-matched levels, the framework achieves a weighted MAE of 0.00165 cm^{-1} . The results demonstrate that a compact residual model can capture transferable spectroscopic structure using interpretable quantum-state and calculation-disagreement features.

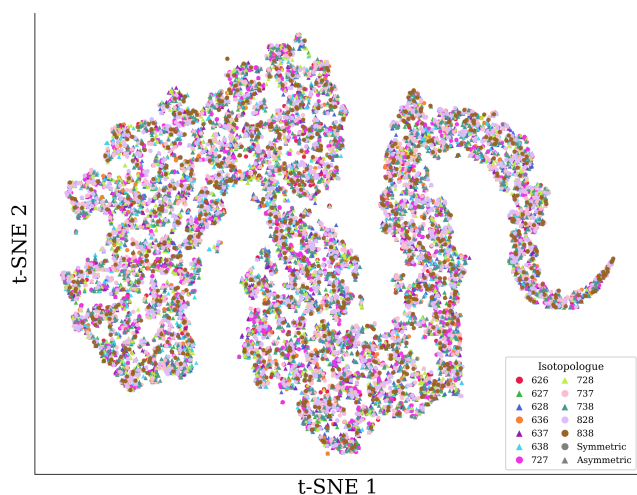


Figure 23: t-SNE projection of the eight-dimensional model feature space for 8,000 rovibrational states. Colors denote CO₂ isotopologues, while circles and triangles indicate symmetric and asymmetric species, respectively. The strong mixing of isotopologues shows that similar states occupy shared feature-space regions, motivating leave-one-isotopologue-out validation rather than conventional random splitting.

E: Invited Speakers

Tuesday, September 01, 2026, 09:00

Chair : Oskar Asvany

BROADBAND VIBRATIONAL SPECTROSCOPY OF MOLECULAR IONS: FROM ASTROCHEMICAL FINGERPRINTS TO REACTION MECHANISMS

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²Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

Molecular ions are key intermediates in gas-phase chemistry, yet their spectroscopic characterization remains challenging due to their high reactivity and low densities. The combination of cryogenic ion trapping with widely tunable infrared free-electron lasers has emerged as a powerful approach to study such species in isolation, yielding vibrational fingerprints of elusive molecular ions, radicals, and transient reaction intermediates with unprecedented structural specificity, ranging from small hydrocarbon ions to protonated complex organic molecules, PAH precursors, and reactive open-shell radicals. Recent examples will be presented from studies of molecular ions relevant to the chemistry of interstellar clouds, photon-dominated regions, and planetary atmospheres, with the goal of linking laboratory spectroscopy to molecular inventories in astronomical environments.

Beyond molecular identification, infrared action spectroscopy has evolved into a versatile tool for probing gas-phase chemical processes. Examples will be presented in which spectroscopic interrogation of trapped ions elucidates low-temperature ion-molecule reactions and their kinetics, while studies of dissociative ionization and fragmentation pathways reveal both the formation and destruction mechanisms of complex molecules. These investigations demonstrate how vibrational spectroscopy, enabled by infrared free-electron lasers, can provide direct insight into molecular structure, reactivity, and chemical evolution in isolated gas-phase systems.

THE SPACE AS A SPECTROSCOPIC LABORATORY: A NEW VIEW OF THE CHEMICAL COMPLEXITY IN THE UNIVERSE WITH THE QUIJOTE LINE SURVEY

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This contribution is devoted to the analysis of chemical complexity in interstellar and circumstellar clouds. In particular, I will present the recent results obtained with the QUIJOTE line survey of the cold dark core TMC-1.

The observations have been carried out with the YEBES (Spain) 40m radio telescope in the Q-band. A new set of receivers have been installed in the telescope within the frame of the ERC synergy Nanocosmos project that allows to cover the whole 31-50 GHz band in dual polarization with a spectral resolution of 38.15 kHz. The survey reaches an unprecedented sensitivity varying between 0.06 and 0.20 mK, and allows to search for new molecules in a line by line (no stacking) detection procedure.

The new data have permitted to detect many protonated species of abundant molecules, several sulfur-bearing species, cycles (benzynes, cyclopentadiene, indene, acenaphthylene -see figure-, phenalene), radicals, and long hydrocarbon chains. I will show the present chemical models we have performed to explain the chemistry of these species and in particular the possible reactions leading to the formation of these cycles. We suggest that a bottom-up approach starting with reactions of simple radicals, such as propargyl and the vinyl radical, with vinyl and allyl acetylene and other hydrocarbons could reproduce satisfactorily well the observed abundances. None of the new molecules found in TMC-1 are detected towards the carbon-rich evolved star IRC+10216.

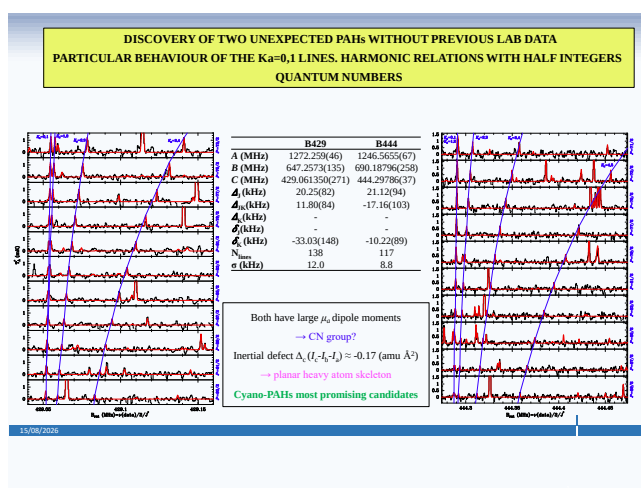


Figure 24: Detection of two new cyano-PAH molecules in TMC-1. They are 1- and 5-cyanoacenaphthylene. 138 and 117 rotational lines were found for these two species. Laboratory spectroscopy confirmed the identification performed from the astronomical data.

F-I: Contributed Talks

Tuesday, September 01, 2026, 11:00

Chair : Marie-Aline Martin-Drumel

AI

DISSECTING INFRARED SIGNATURES IN INTERSTELLAR ICES BY INTEGRATED MATRIX-ISOLATION SPECTROSCOPY AND ANHARMONIC CALCULATIONS

Malgorzata Biczysko¹, Justyna Krupa¹

¹University of Wrocław, Poland

Interstellar ices are considered to provide diverse local molecular environments that favour chemistry leading to the formation and evolution of complex organic and potentially prebiotic species. The high-quality infrared observations delivered by the James Webb Space Telescope (JWST) have substantially advanced the characterization of interstellar ices; however, extracting their full chemical information requires laboratory reference spectra and accurate theoretical modelling capable of resolving the effects of local molecular environments on diagnostic infrared signatures.

In this contribution, complex infrared spectral patterns observed in laboratory analogues of interstellar ices and in JWST observations are investigated using an integrated experimental and computational approach. Low-temperature Matrix Isolation Fourier Transform Infrared (MI-FTIR) spectroscopy combined with controlled co-deposition of ice components enables the formation of molecular complexes and small aggregates that are trapped in inert argon matrices, preserving well-defined local configurations representative of local molecular environments in interstellar ices, where weak intermolecular interactions are expected to reshape diagnostic vibrational signatures. The experimental spectra are interpreted using fully anharmonic vibrational calculations based on second-order vibrational perturbation theory (GVPT2) within a reduced-dimensionality framework, providing reliable predictions of band positions, intensities, and interaction-induced spectral shifts. This combined methodology allows the identification of spectroscopic fingerprints associated with specific aggregation motifs and provides benchmark reference data for the interpretation of astronomical infrared spectra of interstellar ices.

Acknowledgement

This work has been enabled by the financial support from the National Science Centre (NCN), Poland under the SHENG 4 call, project no. 2025/56/Q/ST4/00207 and COST Action CA21101 "COSY - Confined molecular systems: from a new generation of materials to the stars". Computations have been performed at the Wrocław Centre for Supercomputing (wcoss.pl).

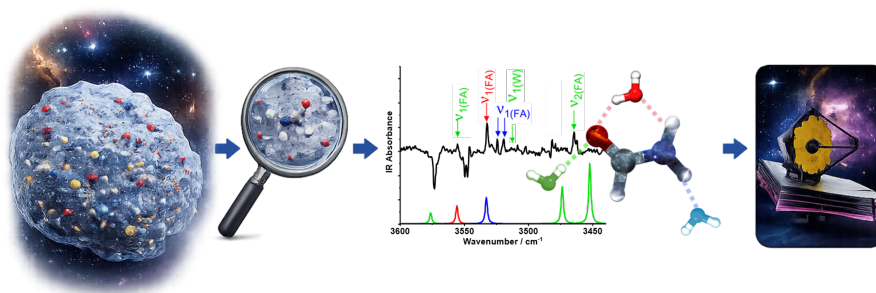


Figure 25: A bottom-up strategy for interpreting infrared spectra of interstellar ices: complex astrochemical environments are dissected into well-defined molecular complexes, allowing individual intermolecular interactions to be identified and the resulting knowledge to be transferred back to realistic interstellar ices.

HIGH-POWER LASER-PLASMA CHEMISTRY OF METHANOL VAPOR AND ITS DEUTERATED ISOTOPOLOGUES: SPECTROSCOPIC APPROACH

Veronika Horká-Zelenková¹, Josef Krása¹, Martina Toufarová¹, Jakub Cikhardt^{2,3}, Vojtěch Scheinpflug^{1,4}, Pooja Devi¹, Shubham Agarwal¹, Norbert Kanaloš¹, Roman Dudžák^{1,3}, Tomáš Burian¹, Michal Krupka^{1,3}, Sushil Singh^{1,2,3}, Libor Juha¹

¹Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic

²Faculty of Electrical Engineering, Czech Technical University in Prague, Prague, Czech Republic

³Institute of Plasma Physics of the Czech Academy of Sciences, Prague, Czech Republic

⁴Department of Physical Chemistry, Faculty of Science, Charles University, Prague, Czech Republic

We investigate the chemical transformation of methanol and its deuterated isotopologues (CH_3OH , CH_3OD , CD_3OH , and CD_3OD) initiated by laser-induced dielectric breakdown (LIDB) plasmas at the high-power iodine laser facility PALS [1]. High-power laser-produced plasmas enable laboratory simulations of high-energy-density events occurring in planetary atmospheres and the interstellar medium (ISM), where methanol is considered an important precursor of complex prebiotic molecules [2,3].

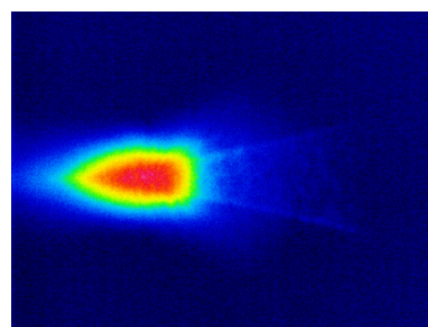
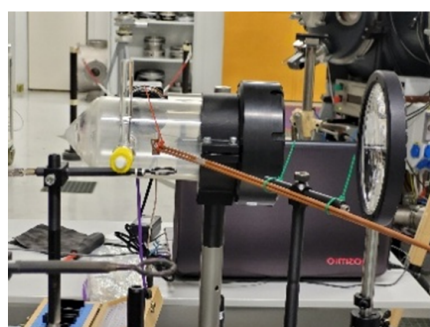


Figure 26: The photograph on the left presents an experimental setup with a lens focusing the laser beam in the middle of a gas cell made of glass; the right image shows a laser spark (diameter 4 cm) created in methanol vapor.

A single 350-ps laser pulse (124–144 J) at a wavelength of 1315.2 nm was focused into a glass cell containing methanol vapor at a pressure of 100 Torr. Typically, four laser pulses were accumulated to achieve sufficient conversion of the reactants into stable final products [4]. The plasma fireball (laser spark) initiates chemical transformations through energetic photons, charged particles, heat, and shock waves emitted from the hot plasma core during the early stage of expansion. The later stage is governed by mixing of the expanding LIDB plasma with the surrounding gas.

Reaction products were analyzed *ex situ* using Fourier-transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry (GC–MS). Initial experiments revealed acetylene (C_2H_2) and its deuterated analogues (C_2HD and C_2D_2) as the dominant reaction products, indicating extensive fragmentation of the parent methanol molecules followed by recombination of small reactive radicals. Ongoing work aims to compare reaction pathways among the deuterated isotopologues to improve our understanding of plasma-induced synthesis of complex organic molecules under conditions relevant to cosmochemistry and molecular astrophysics.

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ANALYSIS OF THE HIGH RESOLUTION INFRARED SPECTRUM OF MONODEUTERO-OXIRANE IN THE 700–1000 CM⁻¹ REGION

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Isotopically chiral oxiranes such as monodeutero-oxirane *c*-C₂H₃DO, *trans*-1,2 dideutero-oxirane (*trans*-*c*-CHDCHDO) and similar molecules^{1 2 3} are of interest in the context of a fundamentally new isotope effect, which arises from the parity violating weak nuclear force^{4 5 6}, and also because of their astro-physical relevance, even as possible chiral tracers for extraterrestrial homochirality as a signature of life⁷. Based on our analysis¹ of the spectrum of *c*-C₂H₃DO in the GHz and THz regions, Müller, et al. reported its detection towards IRAS 16293-2422B in 2023⁸. Here we present results obtained from the analysis of FTIR spectra recorded at Doppler-limited resolution at room temperature with our Bruker IFS 125 HR ETH-SLS 2009 Prototype spectrometer (MOPD = 11.7 m, best possible resolution 0.00052 cm⁻¹)⁹ using a newly synthesized, much improved sample. We have previously reported results of the analysis of the two strongest bands in this region, performed using previous spectra³. Analysis of the new spectra has revealed additional features of the spectrum in this region and has made possible an improved understanding of the observed interactions between the four lowest fundamentals. The results of the analysis will be discussed as they pertain to ab initio calculations^{3 10}, as well as to molecular parity violation, isotopic chirality, and the evolution of biomolecular homochirality^{4 7 11}. We thank G. Matmon for his help with the measurements, the co-authors of previous project publications for their help, and F. Merkt for his support. We have received financial support from ETH, SNF, an ERC Advanced Grant, an SNF-BRIDGE grant, COST MOLIM and COST COSY.

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VIBRATIONAL STARK EFFECT FOR PROBING LOCAL ELECTRIC FIELDS USING LASER SPECTROSCOPY

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Local electric fields (LEFs) are the invisible driving force behind molecular structure, inter-molecular interactions, spectroscopy, and chemical reactivity. Their quantitative characterization therefore represents one of the fundamental challenges in molecular physics. Stark effect describes the modification of a molecule's spectroscopic properties under the influence of an electric field, whether externally applied or generated by its surrounding environment [1]. Such fields can arise in both gas-phase and condensed-phase systems, leading to spectral changes such as shifts or broadening. The Stark effect provides an efficient spectroscopic route for probing LEFs through changes in molecular electronic or vibrational transitions.

This phenomenon can be explored in electronic transitions (referred to as the electronic Stark effect (ESE)) which is particularly valuable for studying UV–Vis chromophores. ESE has been

widely used to probe charge migration processes [1], guide the design of fluorescent sensors [2], and, more recently, enable detailed conformational analysis through field-induced shifts in electronic transitions [3]. Complementarily, the vibrational Stark effect (VSE), defined as the shift in vibrational frequencies of a molecular probe in response to an electric field, provides a highly sensitive measure of the local chemical environment [4]. As such, VSE offers a powerful route to elucidate conformational preferences by correlating structure-dependent electric fields with vibrational frequency shifts.

In this work, we investigate the vibrational Stark effects in a series of benzyl alcohol (BA) derivatives (Figure 1). The hydroxyl group is used as a vibrational probe to evaluate the influence of neutral and charged substituents on the phenyl ring. By combining laser spectroscopy experiments with high-level quantum chemical calculations, we rationalize the relationship between molecular conformation, local electric fields, and vibrational response. Overall, this study in gas-phase demonstrates that VSE analysis provides a robust and sensitive approach to probing with high accuracy subtle environmental effects and their influence on conformational preferences in isolated molecular systems.

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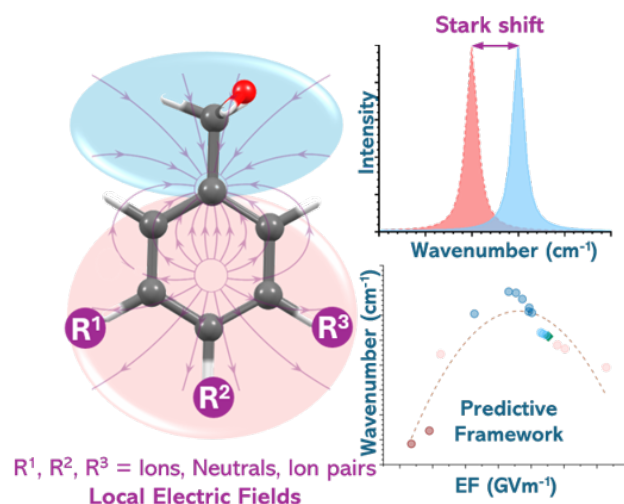


Figure 27: Vibrational shifts of Benzyl Alcohol (BA) derivatives.

OPTICAL FREQUENCY COMB FOURIER TRANSFORM SPECTROSCOPY IN THE 8 μm REGION AND EFFECTIVE HAMILTONIAN LINE LIST OF FORMALDEHYDE

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Formaldehyde (H_2CO) plays an important role as a widely produced industrial chemical and a common atmospheric trace gas originating from combustion and hydrocarbon oxidation, making it an important target for industrial diagnostics and environmental monitoring. In our previous work [1], we measured its high-resolution rovibrational spectrum in the 1250–1390 cm^{-1} (8 μm) region using a mid-infrared optical frequency comb (OFC) combined with a Fourier transform spectrometer (FTS). Our experimental line list was incorporated into a MARVEL [2] analysis, forming the basis for the 2024 update of the HITRAN line list for the main isotopologue $\text{H}_2^{12}\text{C}^{16}\text{O}$ in this range [3].

In this work we extended the measurements to the 1170–1280 cm^{-1} spectral region and provide a more complete assignment of spectra adding two isotopologues. Spectra were recorded at room temperature at four pressures ranging from 0.03 to 2.5 mbar. Spectral analysis was performed line-by-line using a Voigt profile, yielding parameters for 1754 individual transitions spanning four orders of magnitude in line intensity. By combining the new data with our earlier line list, we constructed a unified dataset comprising 2572 experimental transition frequencies and intensities throughout the 1170–1390 cm^{-1} interval. The complete data set is analyzed using a recently developed *ab initio*-based effective Hamiltonian model [4], refined on the experimental data, which enables the assignment of 99% of the observed transitions. This includes both cold- and hot-band transitions of the $\text{H}_2^{12}\text{C}^{16}\text{O}$, $\text{H}_2^{13}\text{C}^{16}\text{O}$, and $\text{H}_2^{12}\text{C}^{18}\text{O}$ isotopologues. Compared to our earlier work [1], where the incomplete theoretical predictions limited the analysis to the main isotopologue, the present model enables a more comprehensive interpretation and assignment. The calculated transition frequencies reproduce the experimental values with a standard deviation of 12 MHz.

This work extends the spectral coverage and isotopic completeness of the formaldehyde line list in the 8 μm region beyond what is currently available in HITRAN and provides an improved basis for spectroscopic modeling and applications in atmospheric, environmental, and astrophysical studies.

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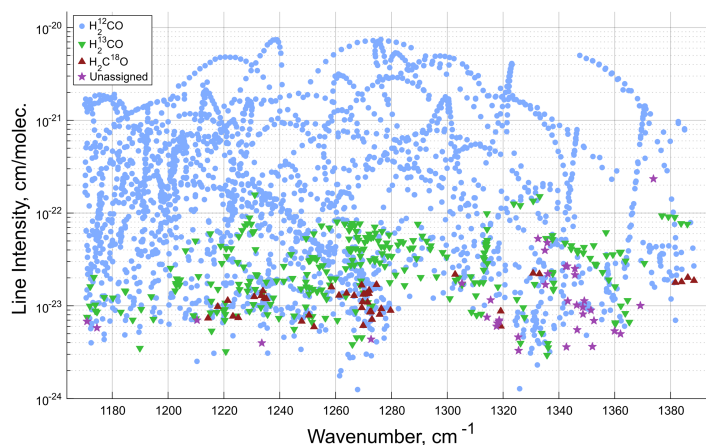


Figure 28: Experimental line intensities in the combined line list of $\text{H}_2^{12}\text{C}^{16}\text{O}$ (light blue circles), $\text{H}_2^{13}\text{C}^{16}\text{O}$ (green triangles), and $\text{H}_2^{12}\text{C}^{18}\text{O}$ (red triangles) assigned using the effective Hamiltonian calculations. The magenta stars show unassigned transitions.

DUAL-FREQUENCY-COMB SPECTROSCOPY FROM THE TERAHERTZ TO THE VACUUM ULTRAVIOLET

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Dual-comb spectroscopy (DCS) is a powerful technique that exploits mutual coherence of the optical frequency combs to enable high-resolution spectroscopic measurements across terahertz to UV frequencies referenced to an atomic clock. By interfering two broadband frequency combs with slightly different comb-line spacing, DCS provides rapid, multiplexed access to precise spectral information across wide bandwidths, simultaneously spanning more than an octave [1]. In the mid-IR to terahertz domain, we implement field-resolved electro-optic sampling [2], enabling the acquisition of high-resolution rovibrational spectra of multiple molecules that have been incorporated into the HITRAN database (e.g., carbon disulfide, methanol, ethanol, isoprene, and dimethyl sulfide) with spectral resolution far exceeding the state of the art.

Most recently, we extended dual-comb spectroscopy into the UV by generating ultrabroadband frequency combs containing up to one million individually resolved comb lines [3], followed by the first demonstrations of high-resolution dual-comb spectroscopy in the deep UV and the development of a vacuum UV frequency-comb source.

Our DCS platform delivers MHz-level spectral resolution and provides a clear pathway to kHz-level resolution across the terahertz to UV regions through comb shifting and subsequent spectral interleaving. Looking ahead, we aim to extend DCS into the vacuum ultraviolet (VUV), <200 nm, opening new opportunities for precision spectroscopy of fundamental systems, including the exotic low-energy nuclear transitions such as the thorium-229 isomer transition at 148 nm wavelength.

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F-II: Contributed Talks

Tuesday, September 01, 2026, 11:00

Chair : Isabelle Kleiner

AII

ROTATIONAL SPECTROSCOPY OF C-DEUTERATED AMINOACETONITRILE AND REFINEMENT OF ITS SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURE

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Aminoacetonitrile is a pivotal species to investigate the formation of prebiotic species in the Interstellar Medium (ISM), as it is considered a possible precursor of the simplest amino acid, glycine. The ground state and some vibrationally excited state emission lines of this molecule have been detected in the ISM toward the hot core of the massive star-forming region Sagittarius B2(N1) in 2008[1] and in 2020[2], respectively. The ro-vibrational spectroscopic characterization of the parent species is available in literature[2, 3, 4], along with studies concerning some isotopologues substituted with ¹³C and deuterium : NHDCH₂CN, ND₂CH₂CN, NH₂CH₂¹³CN, and NH₂¹³CH₂CN[5, 6]. With the aim of completing the analysis of all the possible isotopologues and providing additional sets of rotational constants to improve the semi-experimental equilibrium structure of aminoacetonitrile, in this work we recorded and characterized for the first time the experimental pure rotational spectra of the mono and bis deuterated species NH₂CHDCN and NH₂CD₂CN in the frequency range between 90 and 320 GHz. The spectroscopic parameters relative to the ground state and to the three lowest vibrational states (ν_{18} , ν_{11} , ν_{17}), their overtones ($2\nu_{18}$, $2\nu_{11}$) and their combination states ($\nu_{18}+\nu_{11}$ and $2\nu_{18}+2\nu_{11}$) have been determined with high accuracy for NH₂CD₂CN through a detailed analysis of the Coriolis resonances that perturb these excited states. For the mono deuterated species the spectroscopic parameters relative to the ground state have been determined as well. The new spectroscopic line catalogs provided will be useful to prompt future astronomical searches of these species.

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CONFORMATIONS OF THE MACROCYCLIC LACTONE HABANOLIDE: INFLUENCE OF THE DOUBLE BOND REVEALED BY ROTATIONAL SPECTROSCOPY

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Among odorants, musks have a prominent place within the perfume industry due to their sensual and animalistic smell and are used as base notes in fragrances. Knowledge of their favoured conformations is relevant to achieve a more comprehensive understanding of their molecular recognition processes. However, there is very limited information on the conformations of musks as they are inaccessible by traditional structural techniques. Here, we report the investigation of the 16-membered macrocyclic lactone habanolide (C₁₅H₂₆O₂). Habanolide exists as four regioisomers, 12E, 12Z, 13E and 13Z, which differ in the position (12 or 13) and configuration (*entgegen* or *zusammen*) of the double bond. Analysis of their chirped pulse Fourier transform microwave (CP-FTMW) spectra has allowed the identification of several conformations for each regioisomer. Their distinct conformational landscapes will be discussed, considering the structures of the observed conformations and their intramolecular non-covalent interactions. The results will also be compared to the related 16-membered lactone exaltolide, which is fully saturated, providing overall insight into the influence that the position and configuration of a double bond exerts on the observed conformations of macrocyclic musks.

LARGE AMPLITUDE MOTIONS REVEALED BY FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY IN A POTENT ALKYLATING AGENT: METHYL METHANESULFONATE

Quentin Messaoudi¹, Sven Herbers², Beppo Hartwig², Kenneth Koziol², Ghita Oubouali¹, Guillaume Dhont¹, Ha Vinh Lam Nguyen², Luyao Zou¹

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Methyl methanesulfonate (MMS), $\text{CH}_3\text{SO}_2\text{OCH}_3$, is a flexible sulfonate ester and potent alkylating agent of nucleobases.^{1,2} Its high reactivity with the nucleobases is generally attributed to its small size as a leaving group in the $\text{S}_{\text{N}}2$ nucleophilic substitution reaction. Early theoretical calculations indicated an *anti-gauche* conformational isomerisation potential in a similar system, ethyl methanesulfonate.³ The two conformers of MMS, *anti*- and *gauche*-, have also been identified from low-resolution infrared spectra.⁴ Nevertheless, its internal dynamics, including the effect of large amplitude motions, has not been clearly discussed due to the lack of high resolution spectroscopic data. Each conformer of MMS contains two inequivalent methyl internal rotors.

In this work, we present the first gas-phase rotational spectrum of MMS between 5 and 20 GHz recorded using the jet-cooled Fourier-transform microwave spectrometer PARIS⁵, complemented by theoretical calculations. More than 500 transitions belonging to the ground vibrational states of both conformers have been assigned. The torsional splittings due to the internal rotation of both methyl rotors have been resolved and modelled using XIAM.⁶ We have also discovered some additional splittings that might be associated with a tunneling motion of the *gauche* conformer. Our experimental results agree well with the tunnelling potential obtained from the theoretical calculations. Our work provides a more detailed description of the conformational landscape and internal dynamics of MMS, which may further explain its reactivity in biological systems.⁷

¹Lundin *et al.*, *Nucleic acids research*, 33(12): 3799–3811, 2005.

²Wyatt and Pittman, *Chemical research in toxicology*, 19(12): 1580–1594, 2006.

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⁵H.V.L. Nguyen, S. Herbers, X. Landsheere, J.-U. Grabow, *Rev. Sci. Instrum.* 96, 054706, 2025.

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⁷This work is financed by the ANR-22-CPJ2-0030-01 project

UNEXPECTEDLY LOW METHYL TORSIONAL BARRIERS IN THE MICROWAVE SPECTRUM OF 3-METHYL-2-THIOPHENECARBOXALDEHYDE RESOLVED AFTER A LONG-STANDING SPECTRAL ASSIGNMENT

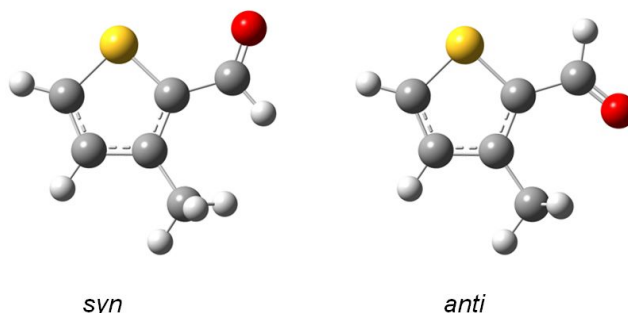
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³Institut Universitaire de France (IUF), F-75231 Paris, France

Large Amplitude Motions (LAMs) are among the most challenging phenomena in rotational spectroscopy, particularly when they interact with conformational flexibility. 3-Methyl-2-thiophenecarboxaldehyde (3M2TPC) is an aromatic sulfur-containing molecule exhibiting two conformers, in which the hydrogen atom of the aldehyde is either in an *anti*- or *syn*-orientation relative to the methyl group adjacent to the aldehyde substituent. The methyl group undergoes LAM internal rotation, causing all rotational transitions to split into A-E doublets. Since the methyl group is sterically hindered by the neighboring aldehyde group, we initially expected the barrier to be intermediate or high, similar to those of *anti*-2-acetyl-3-methylthiophene ($\sim 300\text{ cm}^{-1}$)¹ or *o*-toluic acid ($>1000\text{ cm}^{-1}$).² To our surprise, our many previous attempts to assign its microwave spectrum remained unsuccessful.



Today, we finally report the successful assignment of both conformers using a 6.5–16.5 GHz survey spectrum recorded with a cavity-based Fourier-transform microwave spectrometer called 'the big cavity',³ together with additional measurements from 2–20 GHz obtained using the resonator mode of the PARIS (Passage And Resonance In Synergy) spectrometer.⁴ The spectra were analyzed using the programs *XIAM*⁵ and *westerfit*,⁶ the latter providing significantly improved fits of the experimental transitions. For the *syn* conformer, the methyl torsional barrier is 38.3 cm^{-1} , whereas it is 189.8 cm^{-1} for the *anti* conformer. Both values are remarkably low, especially that of the *syn* conformer, indicating that steric effects alone fail to explain the methyl internal rotation. The barriers are compared with those reported for related aromatic molecules containing a carbonyl (C=O) substituent, providing new insights into the factors controlling methyl internal rotation in heteroaromatic systems.

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³J.-U. Grabow, W. Stahl, H. Dreizler, *Rev. Sci. Instrum.* **67**, 4072 (1996).

⁴H. V. L. Nguyen, S. Herbers, X. Landsheere, J.-U. Grabow, *Rev. Sci. Instrum.* **96**, 054706 (2025).

⁵H. Hartwig, H. Dreizler, *Z. Naturforsch.* **51a**, 923 (1996).

⁶J. H. Westerfield, S. E. Worthington-Kirsch, K. N. Crabtree *J. Mol. Spectrosc.* **404**, 111928 (2024).

THREE METHYL INTERNAL ROTORS OF 3-ACETYL-2,5-DIMETHYLTHIOPHENE INVESTIGATED BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

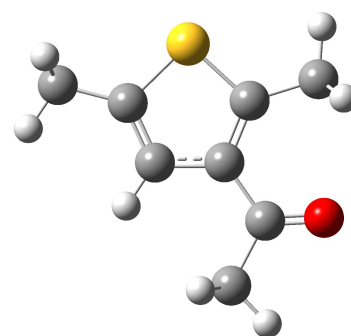
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Methyl internal rotation is one of the most challenging Large Amplitude Motions (LAMs) in rotational spectroscopy. It couples the overall molecular rotation with the methyl torsional motion, leading to complex spectral patterns. When several methyl groups are present, couplings between the methyl groups add a further layer of complexity. Therefore, the number of molecules containing two internal rotors that have been successfully analyzed is already relatively small, and only a handful of molecules with three methyl internal rotors have been studied to date.¹ 3-Acetyl-2,5-dimethylthiophene is a five-membered heteroaromatic molecule featuring three methyl internal rotors, for which each rotational transition is split into fourteen torsional species.



The microwave spectrum of 3-acetyl-2,5-dimethylthiophene was recorded with a cavity-based Fourier-transform microwave (FTMW) spectrometer called „the big cavity“,² together with additional measurements from 2-20 GHz obtained using the PARIS (Passage And Resonance In Synergy) FTMW spectrometer.³ The molecule exists in two conformations, in which the oxygen atom of the carbonyl group is either in an *anti* or a *syn* orientation with respect to the sulfur atom of the thiophene ring. However, only the lower-energy conformer (*syn*) was observed experimentally. Quantum chemical calculations predict torsional barriers of 250 cm⁻¹, 270 cm⁻¹, and 460 cm⁻¹ for the methyl groups at the 2- and 5-positions of the thiophene ring and for the methyl group of the acetyl substituent, respectively. Since two of these barriers are very similar and all barriers are intermediate, the corresponding torsional splittings are small, resulting in severe spectral congestion and making it particularly difficult to disentangle the different torsional species. A preliminary rigid rotor fit of the ground torsional state (000 species) was obtained using 34 rotational transitions, and the assignment of the remaining torsional species is currently in progress.

¹H.V.L. Nguyen, I. Kleiner **2022** *Phys. Sci. Rev.*, 7, 679-726.

²J.-U. Grabow, W. Stahl, H. Dreizler **1996** *Rev. Sci. Instrum.*, 67, 4072-4084.

³H. V. L. Nguyen, S. Herbers, X. Landsheere and J.-U. Grabow **2025** *Rev. Sci. Instrum.*, 96, 054706.

SLIPPERY HANDSHAKES: MICROHYDRATION-DRIVEN EFFECTS IN ENANTIOSPECIFIC INTERACTIONS CAPTURED IN GAS-PHASE CLUSTERS

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Chirality recognition establishes rules for handed interactions that govern structure-function relationships. To investigate such processes, spectroscopic studies of homo- and hetero-configurational pairings in cold, controlled gas-phase ensembles are particularly relevant, as they provide a setting highly compatible with electronic structure theory. Within this framework, the tandem of high resolution rotational spectroscopy and quantum chemical methods affords exceptional precision in resolving increasingly complex molecular topologies and their defining features: structure, intermolecular interactions, and enantiomer-specific aggregation. [1-3] In this contribution, we examine the chiral aggregation trends of selected biosynthetic precursors and show how the progressive addition of only a few water molecules transforms intrinsic molecular recognition into a solvent-mediated process. These results challenge the traditional three-point interaction picture and reveal a richer interplay between hydrogen bonding and molecular flexibility, where water is not merely a spectator but an active participant in chiral molecular recognition, capable of reorganizing the hydrogen-bond network and substantially modifying the energetic landscape governing complex formation. We further discuss how interlocked homochiral environments enable rotational fingerprints of coherent water tunneling dynamics to emerge in such complex topologies.

References:

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Acknowledgements:

This work was funded by the ERC, 101040850 – MiCRoARTiS. We also acknowledge funding by FCT through projects UID/04564/2025, 2023.00840.BD, 2023.10981.CPCA.A2 and 2024.07904.CPCA.A3.

F-III: Contributed Talks

Tuesday, September 01, 2026, 11:00

Chair : Wybren Jan Buma

B11

PERTURBATION OF CO A¹Π BY a³Π SHOULD HAVE BEEN UNDETECTABLE: DETECTION, MECHANISM, AND SURPRISES

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²Doctoral School of the University of Rzeszow, University of Rzeszow, Poland.

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⁸Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Gdansk, Poland.

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¹¹Synchrotron SOLEIL, Orme de Merisiers, St. Aubin, France.

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Diatomic molecules continue to play a central role in high-resolution spectroscopy, astrophysics, and exoplanetary science, where reliable molecular line positions and intensities are essential for the identification and quantitative analysis of species in planetary and interstellar environments [1]. Carbon monoxide is particularly important because its isotopologue-dependent spectra provide sensitive probes of chemical evolution in interstellar clouds and stellar atmospheres [2].

To obtain accurate spectroscopic information, we combine two complementary FT techniques: VUV absorption spectroscopy (SOLEIL synchrotron) [3] and UV-VIS emission spectroscopy (University of Rzeszow) [4]. The observed CO spectra were analysed by a multistate deperturbation treatment based on effective-Hamiltonian modelling and a simultaneous fit of molecular constants and term values [5,6]. This approach yields a consistent description of the rovibronic level structure in the presence of extensive direct and indirect unimolecular interactions.

Particular attention is devoted to the nominally very weak direct A¹Π–a³Π interaction between near-degenerate rovibronic levels belonging to electronic states of the same valence configuration. Because of the extremely small vibrational overlap integral, $\langle a^3\Pi, v' | A^1\Pi, v'' \rangle \approx 10^{-6}$, this interaction would be expected to remain undetectable. However, measurable level shifts and clear intensity signatures indicating this perturbation are found in ¹³C¹⁸O. These observations led us to investigate, for the first time in CO, interference between indirect perturbation pathways, providing a new perspective on the origin of unexpectedly strong spectroscopic effects in multiply perturbed rovibronic manifolds [7].

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THE SPECTRUM OF CrD NEAR 800 nm RECORDED IN CAVITY-ENHANCED ABSORPTION

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A cavity-enhanced absorption spectrum of CrD recorded with a Ti:sapphire frequency comb source and ‘Vernier’ filtering¹ between 763 and 793 nm reveals a complex band to the short wavelength side of the (1-0) band of the $A^6\Sigma^+-X^6\Sigma^+$ system. It is assigned as the origin band of the $B^6\Pi-X^6\Sigma^+$ system on the basis of ground-state combination differences found between transitions spread amongst 79 branches.

The leading parameters for $v=0$ of the $B^6\Pi$ state are $T'_0 = 12942.5 \text{ cm}^{-1}$, $A'_0 = 38.5 \text{ cm}^{-1}$, $B'_0 = 2.74 \text{ cm}^{-1}$ and $\lambda'_{ss} = 0.5 \text{ cm}^{-1}$. The spin-orbit and spin-rotation splittings are rather strange.

The spectrum also reveals hitherto unreported features in the $A^6\Sigma^+-X^6\Sigma^+$ system of ^{52}CrD , including $\Delta J \neq \Delta N$ transitions in the (1-0) band and about 130 lines in the (2-1) band, giving $T'_2 = 13667.40(4)$, $B'_2 = 2.63825(5)$, $\lambda'_{ss} = 1.689(1)$, $\gamma'_2 = 0.6420(2)$.

A further 160 lines have been assigned to A-X (1-0) transitions in the heavier isotopologue, ^{53}CrD . Implementing appropriate strategies to overcome noise from hollow-cathode sputter source seated in the optical cavity proved crucial to the success of the experiment.

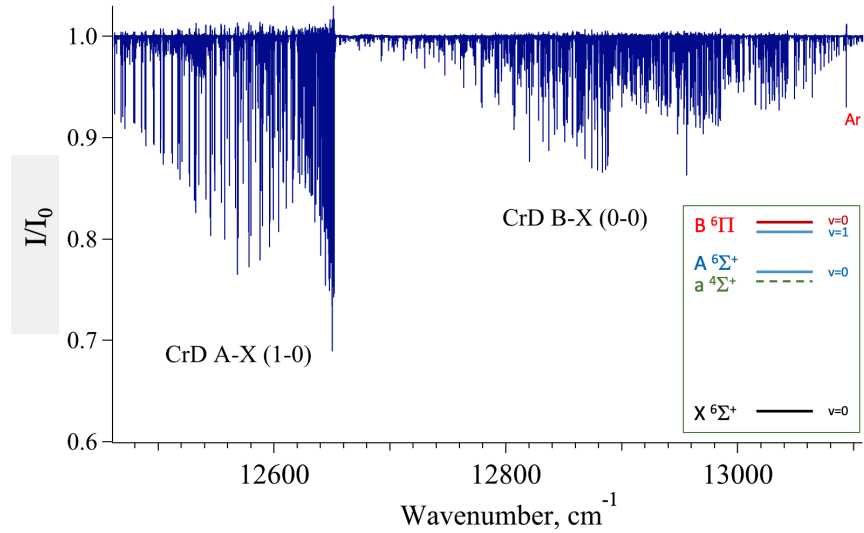


Figure 29: Absorption spectrum of CrD recorded with continuous Vernier filtering, uncorrected for cavity-mirror reflectivity

¹Lu et al Photonics 9 222 (2022)

EXTENSIONS OF ASSIGNMENTS IN THE $F^4\Delta$ - $X^4\Delta$ SPECTRUM OF FeH: LOW- J LINES AND NEW VIBRATIONAL LEVELS

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²University of New Brunswick, Department of Chemistry

³Lyon 1 Université Claude Bernard & CNRS, Institut Lumière Matière

The spectrum of FeH near 1 μm is an important feature in the spectra of sunspots and of cool dwarf stars. It is attributed to the $F^4\Delta$ - $X^4\Delta$ electronic system, which was extensively studied in the laboratory and analyzed in 1987, when transitions involving $v=0, 1, 2$ of both states were observed. The experiments were conducted at the National Solar Observatory (Kitt Peak) in a King furnace at about 2300 °C.

We have extended observations and analysis of this system in two ways, using sources that produce FeH nearer to room temperature:

- We have observed lines at low rotational quantum J missing in the 1987 analysis due to the high temperature of the source.
- We have identified transitions to the $v=3$ levels in both the $F^4\Delta$ and $X^4\Delta$ states.

These new data facilitate identification of new transitions of FeH in solar and astrophysical bodies. In addition they will enable a better determination of potential energy curves for both the $F^4\Delta$ and $X^4\Delta$ states, so that extrapolations of levels to higher temperatures (necessary for comparison with stellar spectra) will have improved accuracy.

COMPETITION BETWEEN PHOTOIONIZATION AND PREDISSOCIATION IN ELECTRONICALLY EXCITED STATES OF He₂ STUDIED BY SIMULTANEOUS DETECTION OF METASTABLE He FRAGMENTS AND He₂⁺ IONS.

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He₂ has been called a "Rydberg molecule" because its ground electronic state is repulsive, whereas its electronically excited states are strongly bound and have Rydberg character [1,2]. In previous studies, only low vibrational levels ($v \leq 3$) of these electronic states have been studied, and almost no information is available on vibrational levels with $v \geq 4$.

We have recently demonstrated that 1+1' two-photon excitation via the $v = 3$ and 4 levels of the $c^3\Sigma_g^+$ state provides access to very high vibrational levels of high-lying Rydberg states of He₂ [3]. In the present work, we introduce an experimental approach to systematically study the high vibra-

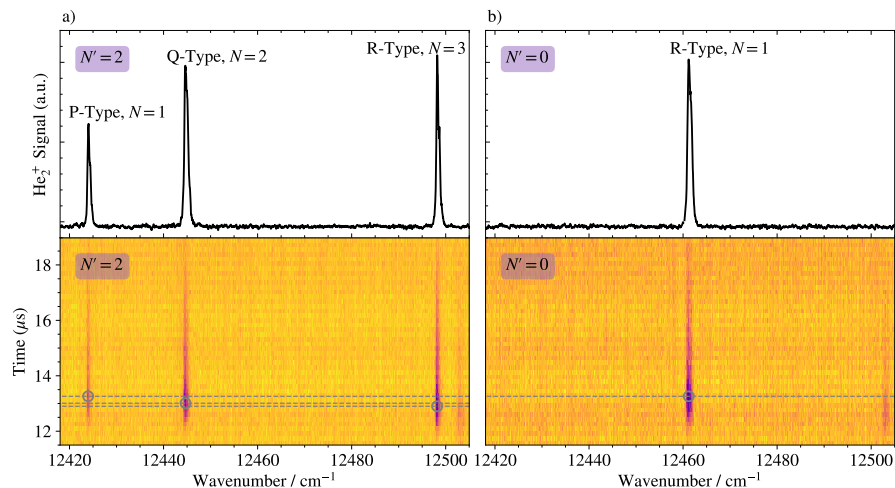


Figure 30: Simultaneously recorded spectra of competing photoionization and predissociation via the $f' ^3\Sigma_u^+(v = 3, N)$ levels of He₂, obtained from the intermediate $c^3\Sigma_g^+(v' = 2, N')$ states with (a) $N' = 2$ and (b) $N' = 0$. In each panel, the upper spectrum corresponds to the He₂⁺ signal produced by (1 + 1' + 1) photoionization, and the lower spectrum corresponds to metastable He* atoms produced by predissociation of the f' state. The maxima in the time-of-flight distributions are marked by gray circles, and dashed gray lines indicate their arrival times.

tional levels of electronically excited states of He₂ using 1+1' excitation via the $c^3\Sigma_g^+$ state. This approach relies on the simultaneous detection of photoionization and predissociation processes.

The well-characterized $c^3\Sigma_g^+(v = 4)$ [3-5] state was used to calibrate the experiment and demonstrate the very efficient detection of tunnelling predissociation in He₂ by monitoring the metastable He(1s2s) ³S₁ fragments on a microchannel-plate (MCP) detector. This detection method was then applied to study transitions to vibrationally excited levels of the $f^3\Sigma_u^+$, $f'^3\Pi_u$, and $d^3\Sigma_u^+$ states. This contribution presents the main results of this study. As an example, the figure displays the spectra of the $f'^3\Pi_u(v = 3, N = 1, 2, 3) \leftarrow c^3\Sigma_g(v = 2, N = 0, 2) \leftarrow a^3\Sigma_u^+(v = 0, N = 1)$ transitions. In both panels, the upper spectrum corresponds to the He₂⁺ signal produced by photoionization, and the lower spectrum corresponds to metastable He* atoms produced by predissociation of the f' state. The maxima in the time-of-flight distributions are marked by open circles, and dashed gray lines indicate the corresponding flight times. The ability to detect dissociation products makes it possible to observe transitions to rapidly dissociating molecular states that cannot be observed by photoionization or laser-induced fluorescence.

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DISENTANGLING FRANCK–CONDON AND HERZBERG–TELLER ACTIVITY IN THE $S_1 \leftarrow S_0$ SPECTRUM OF JET-COOLED STYRENE OXIDE: A COMBINED HIGH-RESOLUTION REMPI AND TDDFT STUDY

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Styrene oxide (phenyloxirane) is a prototypical chiral aromatic molecule that has recently served as a benchmark system for rotational spectroscopy in the millimeter-wave regime¹ and is a promising candidate for the experimental realization of enantiomer-selective IR–mmW three-wave mixing schemes for the determination of enantiomeric excess². Here, we report the vibronically resolved $S_1 \leftarrow S_0$ spectrum of styrene oxide recorded by mass-resolved one-color resonant two-photon ionization (1+1 REMPI) spectroscopy in a supersonic molecular beam. Two complementary experimental setups were employed: a broadly tunable ps-OPG/OPA system combined with an Even–Lavie valve, providing excellent rotational and vibrational cooling and access to the full S_1 band system, and a frequency-doubled dye laser with a General Valve source, offering higher spectral resolution around the electronic origin, located at $37,238\text{ cm}^{-1}$, and revealing additional hot bands. Both data sets are in full mutual agreement. The spectrum exhibits well-defined vibrational progressions reflecting the rigidity of the molecule. All observed bands are assigned on the basis of TDDFT simulations using the ORCA ESD module at the CAM-B3LYP/def2-TZVP level within the adiabatic Hessian approach, including both Franck–Condon and Herzberg–Teller contributions. Particular emphasis is placed on disentangling the Franck–Condon and Herzberg–Teller character of individual vibronic bands and on providing an intuitive, mode-specific rationale for the observed intensity pattern. The complete assignment of the $S_1 \leftarrow S_0$ spectrum establishes a firm foundation for future electronic and double-resonance spectroscopy of this chiral benchmark molecule.

¹Stahl P, Arenas BE, Domingos SR, Fuchs GW, Schnell M, Giesen TF. Laboratory blueprints for interstellar searches of aromatic chiral molecules: rotational signatures of styrene oxide. *Physical Chemistry Chemical Physics*. 2020;22(37):21474-21487. doi:10.1039/d0cp03523h

²Leibsch M, Giesen TF, Koch CP. Principles of enantio-selective excitation in three-wave mixing spectroscopy of chiral molecules. *The Journal of Chemical Physics*. 2019;151(1). doi:10.1063/1.5097406

FIRST ELECTRONIC SPECTRA OF VANADIUM HYDRIDE AND DEUTERIDE (VH/VD)

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¹Macalester College, Department of Chemistry

High-resolution spectroscopy of gas-phase transition-metal radicals provides critical benchmarks for understanding the complex electronic structures of open-shell molecules, enabling stringent tests of quantum chemical calculations and supporting astronomical searches for these species. These open-shell species exhibit rich electronic structure arising from multiple unpaired electrons, leading to unusually complex spectra that challenge both experiment and theory.

We report the first analyses of experimental spectra of gas-phase vanadium hydride (VH) and its deuteride isotopologue (VD), making VH the final member of the 3d transition-metal hydrides to be characterized spectroscopically. Using

laser-induced fluorescence spectroscopy in a hollow cathode discharge source, two electronic transitions of VH (at 654 and 715-nm) and VD have been analyzed. The spectra reveal a $^5\Delta$ ground state with excited states of $^5\Delta$ and $^5\Pi$ symmetry. High spin multiplicity, sparse rotational structure, and extensive local perturbations made these spectra particularly challenging to assign; we describe our deperturbation strategy and effective Hamiltonian modeling approach.

With VH now characterized, we examine periodic trends across the complete 3d transition-metal hydride series, including ground-state symmetries, spin multiplicities, and bond strengths. Because VO and FeH are abundant constituents of cool stellar atmospheres and brown dwarfs, our newly measured VH/VD transition wavelengths provide the laboratory reference data needed to search for vanadium hydride in stellar and exoplanetary atmospheres, particularly in cooler environments where hydrides are expected to become increasingly important relative to oxides.

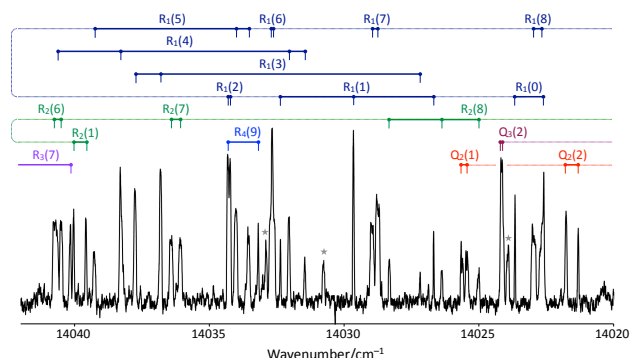


Figure 31: Laser excitation spectrum of the $C'^5\Delta - X^5\Delta (1,0)$ band.

G-I: Contributed Talks

Tuesday, September 01, 2026, 14:00

Chair : Sandra Brünken

AI

MILLIMETER-WAVE SPECTROSCOPY OF CORIOLIS-COUPLED MERCAPTOACETALDEHYDE (HCOCH₂SH)

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²Department of Chemistry, University of Wisconsin-Madison

Mercaptoacetaldehyde (HCOCH₂SH) is the monosulphur analogue of glycolaldehyde, the simplest sugar-related molecule, and was first detected in the interstellar medium towards Sgr B2N by Hollis et al in 2000.^a Interstellar sulphur chemistry remained poorly understood, although an increasing number of complex sulphur-bearing molecules have recently detected, such as thioacetaldehyde (CH₃CHS)^b and ethyl mercaptan (C₂H₅SH),^c along with monothioformic acid (HC(O)SH), which contains both oxygen and sulphur. Mercaptoacetaldehyde is an unstable molecule that exists in its dimer form as 2,5-dihydroxy-1,4-dithiane which decomposes into the monomer following heating to 100-150 °C. Using this method, the microwave spectrum of mercaptoacetaldehyde was measured from 26.5 to 40 GHz, where the low energy conformer is a non-planar twisted structure with *C*₁ symmetry.^d This is in contrast to the hydrogen bond-stabilised planar structure of glycolaldehyde. We have collected the millimeter spectrum of mercaptoacetaldehyde from about 80 to 500 GHz, where we observe significant Coriolis-coupling of the ground state and the first vibrationally excited state (75 cm⁻¹ e). I will present on our progress toward a global least-squares fit of the rotational spectrum of mercaptoacetaldehyde, including treatment of the Coriolis interaction between the ground and first vibrationally excited state. References: a. Hollis, J. M. et al. ApJ, 540 (2000) L107 b. Agúndez, M., et al. A&A, 693 (2025) L20. c. Rodríguez-Almeida et al. ApJL, 912.1 (2021) L11. d. Sung and Harmony, JACS, 99.17 (1977) 5603-5608 e. Yamaguchi, I., et al. J. Mol. Struct., 352 (1995) 309-315.

DETECTION OF S-BEARING SIX-MEMBERED RING IN THE LABORATORY AND IN SPACE

Mitsunori Araki¹, Miguel Sanz-Novo², Christian P. Endres¹, Paola Caselli¹, Víctor M. Rivilla², Izaskun Jiménez-Serra², Laura Colzi², Shaoshan Zeng³, Andrés Megías², Álvaro López-Gallifa², Antonio Martínez-Henares², David San Andrés^{2,4}, Sergio Martín^{5,6}, Miguel A. Requena-Torres⁷, Juan García de la Concepción⁸, Valerio Lattanzi¹

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⁷Towson University

⁸Universidad de Extremadura

Sulfur-bearing molecules are thought to have played a key role in biological processes on Earth. Hence, their detection in space is extremely important for shedding light on the origins of life on Earth. However, predicting interstellar molecules that truly exist in space but have not yet been detected is extremely difficult in a theoretical way. An experimental simulation of the space environment using a discharge allows us to make such a prediction. In 2014, the thiophenoxy radical (C_6H_5S) was produced by a hollow-cathode discharge using thiophenol (C_6H_5SH) [Astron.J. 148, 87, 2014]. This experiment prompted us to investigate ring-shaped molecules in space.

For the astronomical identification, precise laboratory measurements of the thiophenol discharge products system were performed in the 8–40 GHz region using a chirped-pulse Fourier transform microwave spectrometer. These measurements showed not only thiophenoxy radical but also 2,5-cyclohexadien-1-thione (C_6H_6S) and 2,4-cyclohexadien-1-thione, which are structural isomers of thiophenol. The precise rest frequencies were obtained as fingerprints for identifying this organosulfur compound in space. Finally, we astronomically detected a six-membered sulfur-bearing cyclic hydrocarbon in the interstellar medium [Nat.Astron. 10, 401, 2026]. Observations of the Galactic Center molecular cloud G+0.693-0.027 with the Yebes telescope reveal the presence of 2,5-cyclohexadien-1-thione, which now ranks as the largest interstellar sulfur-bearing molecule. The overall results suggest the discovery of a family of prebiotically relevant sulfur-bearing species, which act as a bridge between the chemical inventory of the interstellar medium and the composition of the small bodies in our Solar System that contributed to the formation of planets.

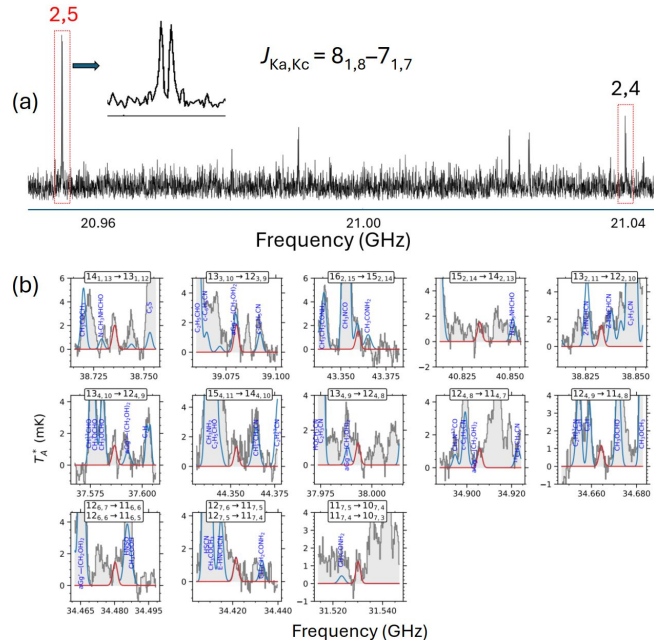


Figure 32: (a) Laboratory spectrum of 2,5-cyclohexadien-1-thione and 2,4-cyclohexadien-1-thione. (b) Detected lines of 2,5-cyclohexadien-1-thione toward the Galactic Center molecular cloud G+0.693-0.693.

MILLIMETER-WAVE ROTATIONAL SPECTROSCOPY OF THIOPHENOL FOR ASTROCHEMISTRY

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¹Max Planck Institute for Extraterrestrial Physics

Molecules containing sulfur are of considerable interest in astrochemistry because of the important role of sulfur in terrestrial biochemistry and the still unresolved inventory of interstellar sulfur-bearing species [1]. In our recent work [2], we reported the detection of 2,5-cyclohexadien-1-thione (c-C₆H₆S), the largest sulfur-containing molecule identified thus far in the interstellar medium, toward the molecular cloud G+0.693–0.027. Thiophenol (c-C₆H₅SH), an aromatic structural isomer of c-C₆H₆S, is energetically more stable and therefore represents a compelling target for astronomical searches.

Thiophenol is a planar aromatic molecule bearing an SH substituent and has already been identified in meteoritic organic material [3]. However, no unambiguous astronomical detection has yet been reported. Searches for thiophenol are complicated by its relatively small dipole moment ($\mu_a = 0.83$ D and $\mu_b = 0.75$ D), the splitting of its rotational spectrum into two torsional substates arising from internal rotation of the SH group relative to the phenyl frame [4], and the previously limited laboratory spectroscopic data available at millimeter wavelengths.

In this work, we extend the laboratory rotational spectrum of thiophenol into the millimeter-wave region by performing room-temperature absorption measurements between 82.5 and 375 GHz. The new measurements increase the available spectroscopic data set from 99 transitions in the previously studied 8–40 GHz region [4] to over ten thousand fitted transitions. A global analysis of the two torsional substates substantially refines the rotational and centrifugal-distortion parameters. Additional higher-order centrifugal-distortion terms were introduced to improve the assignment and maintain accurate frequency predictions over the extended frequency range. The resulting spectroscopic parameters provide a reliable basis for generating millimeter-wave line catalogs and will enable more sensitive astronomical searches for thiophenol.

[1] Z. R. Todd, *Life* 2022, 12, 1268.

[2] M. Araki et al., *Nature Astronomy* 2026, 10, 401–409.

[3] H. Yabuta et al., *Meteoritics & Planetary Science* 2007, 42, 37–48.

[4] N. W. Larsen and L. Schulz, *Journal of Molecular Structure* 2009, 920, 30–39.

ROTATIONAL SPECTRUM AND STRUCTURAL ANALYSIS OF 5-NORBORNENE-2-CARBONITRILE: A BROADBAND MICROWAVE AND MILLIMETER-WAVE MICROWAVE STUDY

Domingo Heras¹, Carlos Cabezas², Isabel Peña¹, Celina Bermúdez¹, Alberto Lesarri¹

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We report the complete rotational characterization of 5-norbornene-2-carbonitrile, a bicyclic nitrile of potential astrochemical relevance, using chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy in the cm- (2–8 GHz) and mm-wave (75–100 GHz) frequency regions. Two conformers, differing in the *exo* or *endo* orientation of the cyano group, have been identified and unambiguously characterized from their rotational spectra.

Rotational constants, centrifugal distortion parameters, and nuclear quadrupole coupling constants have been determined for both conformers. The extension of the dataset into the mm-wave region allowed the precise determination of higher-order sextic centrifugal distortion constants and substantially improved the predictive accuracy relevant for astronomical searches. The experimental parameters are in excellent agreement with geometries and relative energies obtained from DFT calculations at the ω B97X-D and B3LYP levels of theory. All singly substituted ¹³C and ¹⁵N isotopologues have been detected in natural abundance, enabling the determination of a precise experimental ground-state structure for both conformers.

From an astrochemical perspective, 5-norbornene-2-carbonitrile presents several characteristics that make it a compelling candidate for interstellar detection. The cyano group is among the most abundant and widely detected functional groups in the interstellar medium, and structurally related nitriles—including benzonitrile, indene derivatives, and other cyclic species—have been identified in cold dense clouds and star-forming regions such as TMC-1. The structural rigidity of the norbornene bicyclic scaffold, combined with the appreciable dipole moments, results in a favourable rotational spectrum characterized by relatively strong, well-separated transitions accessible to current radiotelescope facilities.

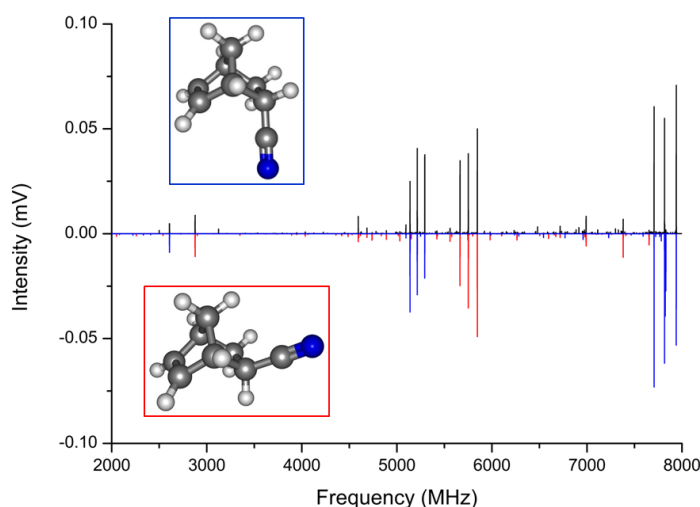


Figure 33: Molecular structures of the *exo* and *endo* conformers of 5-norbornene-2-carbonitrile together with a representative section of the experimental rotational spectrum recorded by CP-FTMW spectroscopy.

ROTATIONAL SPECTROSCOPY OF CYANOCYCLOPENTADIENE ISOMERS AND DIAZOCYCLOPENTADIENE FOR ASTRONOMICAL SEARCH IN HOT INTERSTELLAR MEDIUM

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The recent detection of 1- and 2-cyanocyclopentadiene^{1,2} (cyano-CPD) isomers in the Taurus Molecular Cloud (TMC-1) has highlighted their significance as potential precursors to larger polycyclic aromatic hydrocarbons (PAHs). However, existing laboratory data for these species were largely restricted to the centimeter and early millimeter-wave domain, leading to significant frequency uncertainties when extrapolated to higher frequencies. This study provides an extended spectroscopic analysis of both isomers in the 75–500 GHz range to support astronomical searches in warmer environments. Using the Lille FLASH spectrometer³ and pyrolysis, we synthesized the isomers and analyzed the spectra of 1- and 2-cyano-CPD. These measurements enabled the determination of refined rotational and higher-order centrifugal distortion constants, including sextic and octic terms. Ro-vibrational partition functions⁴ were calculated up to 300 K to assist in accurate column density determinations. Finally, we use these catalogs to search for cyano-CPD isomers in ISM, and we examine whether the local thermodynamic equilibrium assumption is valid in warm environments.

¹McCarthy et al., *Nature Astronomy*, 2020.

²K. Lee et al., *ApJ Letters*, 2021.

³Motiyenko et al., *Review of Scientific Instruments*, 2020.

⁴Gordy and Cook, Wiley-Interscience, 1984.

INVESTIGATING THE PRESENCE OF LARGER CYANO-DERIVATIVE PAHS IN THE INTERSTELLAR MEDIUM

Carlos Limeres Vazquez¹, Megan A. Crutchfield², Carlos Cabezas³, Pablo Jurado², Farha S. Hussain², José R. Morán², Isabel Peña², Alberto Lesarri², Celedonio M Alvarez², Dolores Pérez¹, José Cernicharo³, Cristóbal Pérez¹, Amanda L. Steber²

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With the ever-increasing inventory of detected polycyclic aromatic hydrocarbon (PAH) derivatives in the cold dark molecular cloud TMC-1, the push to flush out this inventory and understand the role of these PAHs has grown[1]. The recent detections of cyanopyrene[2,3] and cyanocoronene[4] indicate the importance of targeting PAHs with four or more rings, as they are detectable with radio astronomy, despite the potential low abundances of such species along with potential partition function dilution. Thus, we have undertaken efforts to synthesize, characterize, and detect the isomers of the four-ring, chiral species cyano[4]helicene and the six-ring, bowl-shaped cyanocorannulene. After the synthesis of both species, we used chirped-pulse Fourier transform microwave spectroscopy from 2-18 GHz to probe the rotational spectrum of each of the species. Upon detection in the laboratory, we performed a search in TMC-1 with the QUIJOTE survey.

[1] Marcelino Aguundez and Jose Cernicharo, 2026 *ACS Earth Space Chem.* **10**,1345

[2] Gabi Wenzel et al., 2024 *Science* **386**,810

[3] Gabi Wenzel et al., 2025 *Nat Astron* **9**, 262

[4] Gabi Wenzel et al., 2025 *ApJL* **984** L36

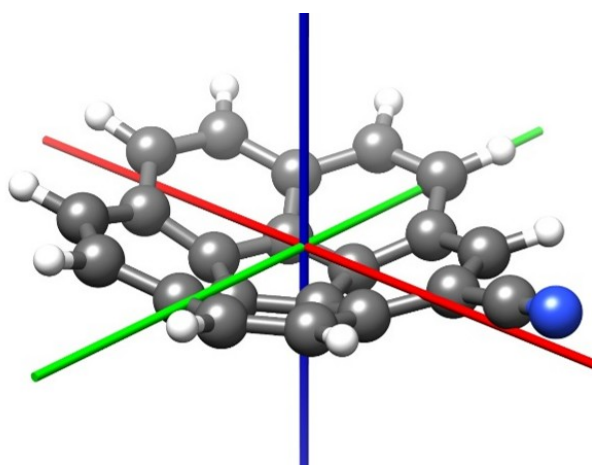


Figure 34: Structure of cyanocorannulene calculated at the B3LYP/def2TZVP level of theory with the GD3BJ dispersion corrections.

FLASH VACUUM PYROLYSIS OF 1-METHYLCYCLOBUTANOL: INSIGHTS FROM ROTATIONAL SPECTROSCOPY

Lucie Kolesníková¹, Karel Vávra¹, Marie Kříž¹, Jan Svoboda¹, Patrik Kania¹, Štěpán Urban¹,
Jean-Claude Guillemin²

¹University of Chemistry and Technology, Prague, Department of Analytical Chemistry, Prague, Czechia

²Univ. Rennes, École Nationale Supérieure de Chimie de Rennes, Rennes, France

Flash vacuum pyrolysis is a powerful technique for the laboratory generation of reactive species from suitable precursors. Many of these transient species are believed to play important roles as intermediates in atmospheric, combustion, and interstellar chemistry. Spectroscopic monitoring of pyrolytic processes is essential for understanding ongoing chemical reactions, identifying reactive species, and optimizing their production. Of the available methods, rotational spectroscopy is uniquely suited for this purpose because it enables the unambiguous identification of individual components in complex gaseous mixtures. In this work, millimeter-wave rotational spectroscopy is employed to track the reactant and principal pyrolysis products of 1-methylcyclobutanol in the gas phase, with the aim of spectroscopically characterizing astrophysically significant 2-propenol and conducting related kinetic studies. The spectroscopic results can be used to interpret radioastronomical data.

ROTATIONAL STUDY OF 1-AMINO-2-PROPANOL AND ITS VIBRATIONAL SATELLITES

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Rotational spectroscopy has played a vital role in identifying most of the approximately 350 molecules detected in space.¹ Ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$), recently identified in the molecular cloud G+0.693–0.027², is one such complex organic molecule. The addition of a methyl (CH_3) group to ethanolamine forms 1-amino-2-propanol (1-a-2-p, $\text{NH}_2\text{CH}_2\text{CH}_2(\text{OH})\text{CH}_3$), a promising candidate for future astronomical detection. A previous rotational spectroscopic study investigated the lowest-energy conformer of 1-a-2-p (a. in Figure 1), in the frequency range of 26.5–39.7 GHz using conventional absorption spectroscopy. It reports the internal rotation barrier height of the methyl group and the spectroscopic rotational constants of the ground and vibrationally excited states.³

This work expands upon the previous study by extending the measured frequency range and providing accurate quartic and sextic centrifugal distortion constants. The rotational spectra of 1-a-2-p were recorded using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the frequency ranges of 12–26.5 GHz and 75–110 GHz⁴ using home-built spectrometers. This approach provides broadband, high-resolution rotational spectra with high sensitivity.⁵ Measurements were performed at ~ 10 K in the lower-frequency range using a supersonic jet expansion and at ~ 300 K in the higher-frequency range.

In addition to the lowest-energy conformer of 1-a-2-p (a. in Figure 1), a second conformer (b. in Figure 1), predicted to be 4.9 kJ/mol higher than the previously reported conformer, has been observed for the first time in this study. The rotational constants for both the ground and vibrationally excited states of both conformers were determined and will be presented. Additionally, nuclear quadrupole hyperfine splitting arising from the ^{14}N nucleus was resolved in the lower-frequency range measurements. These high-resolution spectra for 1-a-2-p will help search for it in astrophysical environments.



Figure 35: Two conformers of 1-a-2-p

¹<https://cdms.astro.uni-koeln.de/>

²Rivilla V. M., et al., Proceedings of the National Academy of Sciences, **2021**, 118.22, e2101314118.

³Marstokk K.-M., and Møllendal H., Journal of Molecular Structure, **1976**, 35.1, 57–66.

⁴Hermanns M. et al., Review of Scientific Instruments, **2023**, 94.3, 034705.

⁵Park G. B. and Field R. W., The Journal of Chemical Physics, **2016**, 144.20, 200901.

G-II: Contributed Talks

Tuesday, September 01, 2026, 14:00

Chair : Sonia Melandri

AII

CHAINING 4H-PYRAN-4-ONE: CONCERTED WATER DYNAMICS IN A PLANAR AROMATIC MOLECULE

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Water plays an essential role in regulating most biochemical processes that are fundamental to life, from protein folding and molecular assembly to molecular recognition [1]. The underlying mechanisms governing these complex condensed-phase scenarios can be decrypted by investigating isolated water-solute clusters in the gas phase [2,3].

In this scope, we investigated the stepwise growth of the solvation layer of 4H-Pyran-4-one (4PN) using broadband rotational spectroscopy in the cold, isolated conditions of a supersonic jet expansion. Being a simplified mimic for many biologically relevant aromatic molecules, 4PN comprises three competing sites for micro-hydration: a carbonyl group, a ring oxygen, and a conjugated π system. Our results show that water has a clear preference for the C=O group, building a three-body chain that wraps around 4PN by establishing secondary interactions with its H atoms. By relying on isotopic data to determine key atomic positions and deploying extensive quantum chemistry calculations, a concerted large amplitude motion of the water chain emerges. In this contribution we will also discuss the importance of transition state optimizations to describe these vibrationally-averaged structures and how these complex dynamic frameworks can be best understood by considering multiple imaginary modes which are often overlooked.

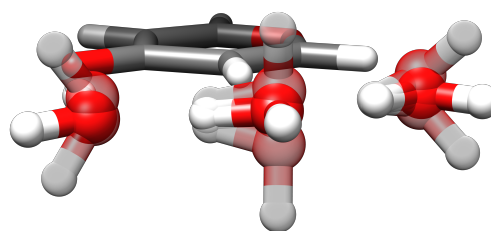


Figure 36: Large amplitude motion in tri-hydrated 4H-Pyran-4-one.

References

- [1] M. Chaplin, M. *Nat. Rev. Mol. Cell Biol.* 2006 7, 861–866.
- [2] W. Li et al. *J. Am. Chem. Soc.* 2023, 145, 4119–4128.
- [3] A.L. Steber et al. *J. Am. Chem. Soc.* 2025, 147, 19568–19574.

Acknowledgements

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NON-LINEAR BIFURCATED HYDROGEN BONDS IN A PROTON SPONGE–FORMIC ACID COMPLEX REVEALED BY ROTATIONAL SPECTROSCOPY

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Donor bifurcated hydrogen bonds occur when a single hydrogen atom of an X–H group interacts simultaneously with two acceptor sites. Such non-linear bifurcated hydrogen bonds have been observed in condensed-phase systems and ionic clusters (e.g., proteins and zwitterions), where local electrostatic stabilization and charge delocalization play a key role. However, their occurrence as stable local minima in isolated gas-phase systems remains rare, and it is still unclear whether this rarity reflects intrinsic energetic limitations of the hydrogen bond network or the lack of a geometrically favorable local environment.

To address this issue, we employed chirped-pulse Fourier-transform microwave spectroscopy to investigate the rotational spectrum of the 1,8-*bis*(dimethylamino)naphthalene (DMAN)–formic acid (FA) complex, where DMAN is predicted to provide a geometrically favorable environment for the formation of bifurcated hydrogen bonds. The experimentally determined rotational constants and resolved hyperfine splittings provide definitive evidence for an intermolecular bifurcated hydrogen bond motif. In this complex, DMAN–FA adopts an asymmetric bifurcated hydrogen bond configuration, featuring one strong primary hydrogen bond and a weaker secondary hydrogen bond. The N $\cdots$ H $\cdots$ N angle is approximately 80°, indicating a markedly non-linear hydrogen bond geometry. Quantum-chemical calculations identify the bifurcated configuration as a local minimum on the electronic potential energy surface. Although zero-point vibrational corrections place this structure as the second-lowest minimum, this conformer persists as one of the major species under supersonic jet expansion conditions. The rotational spectra display no dynamic exchange between the three-center hydrogen bond over the experimental timescale. This study reveals that, under geometrically favorable conditions, hydrogen bond topologies intrinsically adopt non-linear, bifurcated configurations in the gas phase, without reliance on external stabilization.

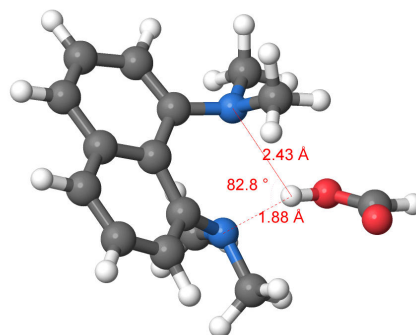


Figure 37: Bifurcated hydrogen-bond geometry of the DMAN–FA complex.

FROM TRIMER TO PENTAMER: STRUCTURAL MOTIFS AND INTERACTIONS IN SO₂ AGGREGATES

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Sulfur dioxide is a common pollutant released into the Earth's atmosphere through natural and anthropogenic means such as volcanic eruptions and fossil fuel burning. It plays a vital role in aerosol nucleation and the formation of cloud condensation nuclei. SO₂ is also found in the interstellar medium and in the atmospheres of Venus and Jupiter's moons Io and Europa. Characterising the growth pathways and interactions of pure SO₂ clusters is essential to understanding the various processes in which SO₂ participates. Using a combination of broadband rotational spectroscopy and quantum chemical calculations, we have observed pure (SO₂)_{3–5} clusters, and determined their structures and non-covalent interactions. Aggregation of SO₂ is governed by multiple S–O · · · S chalcogen bonds which are modulated as the size of the cluster increases. Benchmarking of quantum mechanical methods and a possible aggregation pathway will be discussed.

REVEALING THE STRUCTURE AND INTERMOLECULAR INTERACTIONS OF 2-MERCAPTOETHANOL DIMERS BY BROADBAND ROTATIONAL SPECTROSCOPY

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³Oportunus. Axencia Galega de Innovación, 15702 Santiago de Compostela, Spain

The balance between $\text{O-H} \cdots \text{O}$, $\text{O-H} \cdots \text{S}$, $\text{S-H} \cdots \text{O}$, and $\text{S-H} \cdots \text{S}$ intermolecular interactions plays a central role in determining the structures and stability of sulfur-containing molecular aggregates. As one of the simplest stable molecules containing both hydroxyl and thiol functional groups, 2-mercaptoethanol (2-ME) provides an ideal model system for investigating how oxygen- and sulfur-based hydrogen bonds compete and cooperate in molecular self-association.

The rotational spectrum of the 2-ME monomer has previously been characterized in both the microwave and millimeter-wave regions.^{1,2} However, little is known about the intermolecular interactions governing the aggregation of this molecule.

In this work, we investigate the dimers of 2-ME using broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the 2–8 GHz frequency range, complemented by high-level quantum chemical calculations. Several dimeric species were identified and structurally characterized, revealing the preferred hydrogen-bonding motifs and the delicate balance between O–H and S–H interactions that governs the assembly of the dimers. The experimental structures provide direct insight into the role of sulfur in hydrogen-bond networks and the influence of competing intermolecular interactions on molecular aggregation.

Beyond their intrinsic interest in noncovalent chemistry, these results contribute to our understanding of the aggregation of sulfur-containing complex organic molecules and provide benchmarks for theoretical descriptions of sulfur-mediated interactions.

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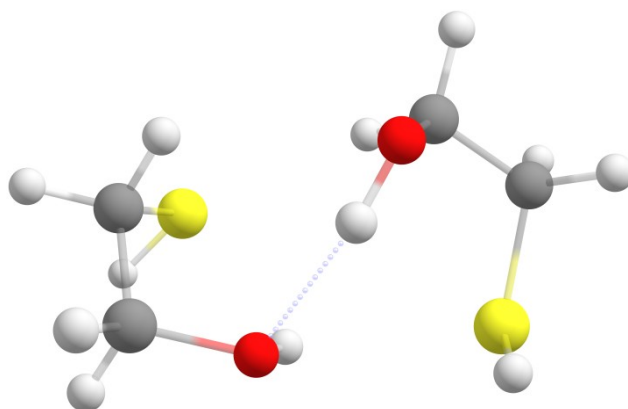


Figure 38: The global minima of 2-ME dimer optimized at B3LYP-D3BJ-def2-TZVP level of theory.

UNVEILING THE UNDERAPPRECIATED: THE BONDING FEATURES OF C–H · · · S–S INTERACTIONS OBSERVED FROM ROTATIONAL SPECTROSCOPY

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The C–H · · · S–S interactions are fundamentally important to understand the stability of bio-macromolecules and their binding with small molecules, but they are still underappreciated. Herein, we characterized the C–H · · · S–S interactions in model molecular complexes. The rotational spectra of the complexes of diethyl disulfide with CH₂CH₂, CH₂CHF and CH₂F₂ were measured and analyzed. The rotational spectrum was collected using a COBRA pulsed-jet Fourier transform microwave spectrometer[1,2], and the observed rotational transition frequencies were fitted using the SPFIT code from the CALPGM suite of programs[3]. All detected structures are dominantly stabilized by a C–H · · · S–S hydrogen bond, achieving stabilization energies of 3.0–7.6 kJ/mol^{−1}. Incidental C–H · · · π or C–H · · · F interactions might further enhance the stability of the complexes. Mainly London dispersion, which accounts for 53%–68% of the total attractions, is the driving force of stabilization.

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WATER- AND FORMIC ACID-ASSISTED CLAISEN REARRANGEMENTS PROBED BY ROTATIONAL SPECTROSCOPY

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The Claisen rearrangement, first reported by Rainer Ludwig Claisen in 1912,^[1] is one of the most fundamental and classical examples of a [3,3]-sigmatropic pericyclic reaction. Hydrogen-bonding solvents such as water and formic acid have been recognized to dramatically accelerate reaction rates,^[2–5] yet direct molecular-level evidence for how such solvents affect the reaction barrier has remained scarce. Here, broadband chirp-polarization Fourier transform microwave (CP-FTMW) spectroscopy,^[6] combined with quantum-chemical calculations, was employed to characterize the Claisen rearrangement of allyl phenyl ether (APE) to 2-allylphenol (2-AP) under solvent-free, water-assisted, and formic-acid-assisted conditions, both with and without heating. Four conformers of APE and APE-(H₂O)_{1–3} hydrates were spectroscopically resolved. The rearrangement product was detected only in the presence of water and at elevated temperature, and transition-state calculations showed that stepwise hydration progressively lowered the activation barrier. To assess the effect of a stronger hydrogen-bond donor, APE complexes with formic acid were further characterized, revealing a stronger hydrogen bond than in the APE–water complexes and a more substantially reorganized conformational landscape, thus yielding two distinct conformers of the product 2-AP rather than one. Product formation again required elevated temperature. These observations demonstrate that the Claisen rearrangement reaction is not governed by a single factor but rather by a cooperative mechanism in which hydrogen-bond-stabilized pre-reaction complexes and transition states act in concert with thermal activation. This work provides molecular-level insight into solvent-assisted sigmatropic rearrangements and establishes a general framework for understanding the interplay of non-covalent interactions and thermal activation in pericyclic reactivity.

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HIGH-RESOLUTION ROTATIONAL SPECTROSCOPY OF $(\text{OCS})_n-(\text{H}_2\text{O})_m$ CLUSTERS

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Intermolecular interactions play an important role in determining the structures and properties of weakly bound molecular clusters. High-resolution microwave spectroscopic studies of OCS homoclusters have revealed diverse aggregation structures governed by a delicate balance of electrostatic and dispersion interactions [1]. Carbonyl sulfide (OCS) and water are important small molecules in atmospheric and interstellar environments. Investigating their weakly bound clusters provides insight into hydration, molecular aggregation, and the early stages of cluster formation.

In this work, high-resolution chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy was employed to investigate the rotational spectra of several $(\text{OCS})_n-(\text{H}_2\text{O})_m$ aggregates. Low-energy structures of each system were explored using the conformer-rotamer ensemble sampling tool (CREST), followed by quantum-chemical geometry optimizations and relative-energy calculations. Accurate spectroscopic constants for $\text{OCS}-(\text{H}_2\text{O})_2$, $(\text{OCS})_2-\text{H}_2\text{O}$, and $(\text{OCS})_3-\text{H}_2\text{O}$ were obtained through the assignment and fitting of the observed rotational transitions, and the experimental results were compared with quantum-chemical predictions to identify the most plausible structures.

The results show that these clusters are stabilized by a combination of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between water molecules, $\text{O}(\text{H}_2\text{O})\cdots\text{S}(\text{OCS})$ contacts, and dispersive interactions between OCS molecules. In addition, some of the investigated $(\text{OCS})_n-(\text{H}_2\text{O})_m$ clusters exhibit distinctive spectral features associated with low-frequency intermolecular vibrations and large-amplitude motions. This study provides new high-resolution spectroscopic data for understanding the structural evolution of mixed OCS–water clusters and the competition among different types of weak intermolecular interactions.

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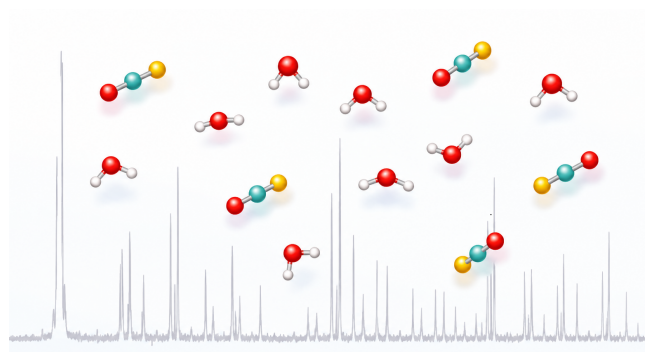


Figure 39: Microwave Investigation of $\text{OCS}-\text{H}_2\text{O}$ Clusters.

DISENTANGLING HYDROGEN VS. CHALCOGEN BONDING IN $(\text{HCl})_2 - \text{H}_2\text{S}$ AND $\text{HCl} - \text{H}_2\text{O} - \text{H}_2\text{S}$ TRIMERS VIA BROADBAND ROTATIONAL SPECTROSCOPY

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The delicate balance between competing non-covalent interactions—conventional hydrogen bonding versus chalcogen and halogen bonding—dictates the structural motifs of hydrogen halide–chalcogenide clusters. Here we report the laboratory detection and rotational characterization of two novel ternary complexes, $(\text{HCl})_2 - \text{H}_2\text{S}$ and $\text{HCl} - \text{H}_2\text{O} - \text{H}_2\text{S}$, using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in a supersonic expansion. Rotational spectra for multiple isotopologues were assigned, yielding accurate rotational and centrifugal distortion constants that establish the gas-phase geometries. Chlorine nuclear quadrupole coupling tensors (χ_{aa} , χ_{bb} , χ_{cc}) serve as a sensitive local probe of the bonding environment, allowing the two binding sites to be distinguished without relying solely on theoretical predictions. Notably, despite the polarizable, Lewis-basic character of sulfur, no $\text{S} \cdots \text{Cl}$ contact is observed in $(\text{HCl})_2 - \text{H}_2\text{S}$: both HCl subunits instead act as cooperative hydrogen-bond donors to sulfur, mirroring the cyclic structure of $(\text{HCl})_2 - \text{H}_2\text{O}$. Comparing this trimer series, $(\text{HCl})_2 - \text{H}_2\text{O}$, $\text{HCl} - (\text{H}_2\text{O})_2$, $(\text{HCl})_2 - \text{H}_2\text{S}$, and $\text{HCl} - \text{H}_2\text{O} - \text{H}_2\text{S}$, shows that cluster topology, more than acceptor identity (O vs. S), governs the cooperativity and charge transfer. Overall, conventional hydrogen bonding, not chalcogen bonding, remains the dominant organizing interaction in these systems, even for the more polarizable sulfur acceptor.

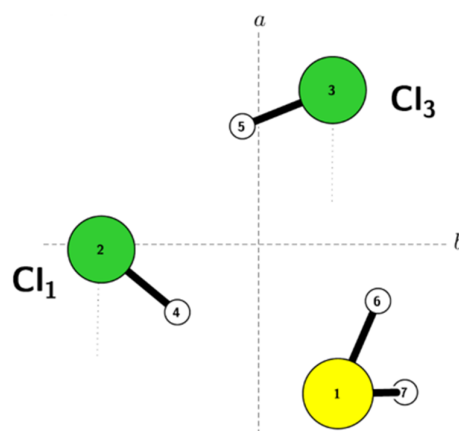


Figure 40: r_0 structure of the $(\text{HCl})_2 - \text{H}_2\text{S}$ trimer.

G-III: Contributed Talks

Tuesday, September 01, 2026, 14:00

Chair : Dennis Tokaryk

B11

SPECTROSCOPY OF MOLECULES, RADICALS, AGGREGATES BASED ON SILICON AND HYDROGEN

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In the context of quantum computer development, silicon ^{28}Si is essential for ensuring sufficient coherence time of qubits. Laser separation of ^{28}Si using a supersonic cold molecular jet is being considered with SiH_4 . To initiate this study, we have chosen to work on the silane molecule¹ and its isotopologues, with the objective of creating a spectroscopic database. This database will provide the Hamiltonian parameters of line positions and intensities, using the tensor formalism and the tools developed by the Dijon research group.

Four different frequency regions were studied including all the fundamental bands and many other combination bands, ν_2/ν_4 are included in the new SiCaSDa database². The experimental measurements were carried out at Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) in Créteil, Paris. These results may also be applied in the field of astrophysics, where the presence of silane has been detected in the interstellar medium.

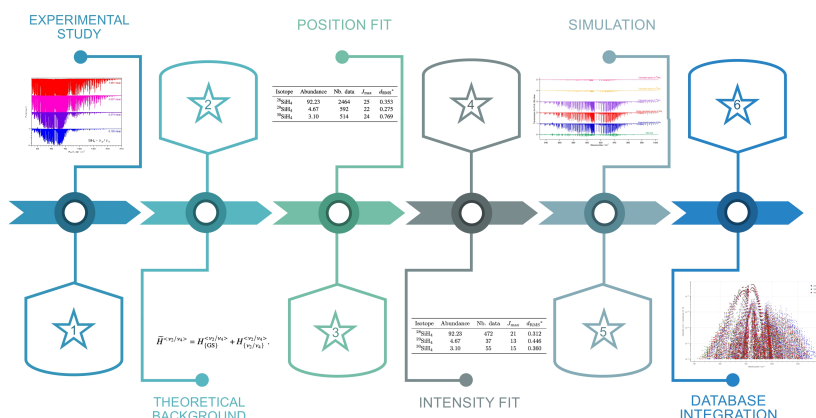


Figure 41: Methodology used for spectra analysis.

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INFRARED SPECTROSCOPY OF ACETALDEHYDE IN SUPERFLUID HELIUM NANODROPLETS IN THE 3-MICRON REGION

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Helium nanodroplet isolation (HENDI) spectroscopy offers a weakly perturbing ultracold environment that enables high-resolution spectroscopic studies of molecules and molecular clusters¹. Following the recent upgrade of our HENDI spectrometer, including the integration of an electrospray ionization (ESI) source and a quadrupolar linear ion-trap², acetaldehyde CH₃CHO was investigated for initial evaluation of the apparatus performance, and for its importance in astrochemistry, atmospheric photochemistry, and biological metabolism.

Although the rotational spectrum of acetaldehyde has been extensively studied³, only limited assignments have been reported for its infrared spectrum⁴ in the C–H stretching region and a concrete assignment is lacking because of significant anharmonicity⁵. Here, infrared spectra of acetaldehyde were recorded in the 3 μ m region under varying pickup conditions, which indicate contributions from monomers, dimers, and larger clusters. The mass-selected infrared (MSIR) measurements obtained with a quadrupole mass spectrometer enabled separation of monomer and cluster dominated spectral features, allowing clear differentiation between monomer and dimer sensitive spectral features. High-precision anharmonic vibrational simulations based on the discrete variable representation approach⁶ were performed which provide firm assignments of the observed monomer bands whose assignments differ from those reported in the previous gas phase and matrix isolation studies. Furthermore, spectral features of the dimer were identified and tentatively assigned based on the corresponding dimer anharmonic simulations. The role of anharmonicity in the C–H stretching region of the monomer and dimer will be discussed.

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LINE INTENSITIES AND SELF-BROADENING COEFFICIENTS FOR THE ν_{14} BAND OF PYRROLE NEAR 14 μm

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The detection and quantification of trace gases in planetary atmospheres using optical remote sensing techniques require that appropriate spectroscopic reference data be available. The present contribution is part of a project aiming to provide missing or improved spectroscopic information for species selected for their potential relevance in planetary atmospheres. The target spectral region is the 600 – 2000 cm^{-1} range (16.5 to 5 μm), chosen for its relevance to current and future space missions.

The present study is a high-resolution investigation of the strong ν_{14} band of pyrrole ($^{12}\text{C}_4\text{H}_5^{14}\text{N}$), observed near 14 μm . It was chosen because it was predicted to be the strongest of the 24 fundamental bands of the molecule [1] and it is located in the above-mentioned spectral range. Building upon our recent contribution [2], its main objective was to provide intensity information for this vibrational band for the first time.

Five Fourier transform infrared absorption spectra of pure pyrrole were recorded at room temperature and pressures between 0.32 and 1.9 hPa, with an absorption path length of 19.7(2) cm and a spectral resolution of 0.0015 cm^{-1} . Line intensities and self-broadening coefficients were measured using a multi-spectrum fitting technique. The rotational dependence of the corresponding vibrational transition dipole moment squared and of the measured self-broadening coefficients were studied [3]. Results will be presented and discussed.

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NEW SPECTROSCOPIC LINE PARAMETERS OF H₂O IN THE FAR-INFRARED REGION FOR ESA'S FORUM MISSION

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The upcoming ESA FORUM (Far-infrared Outgoing Radiation Understanding and Monitoring) mission will be the first to measure the Earth's spectrally resolved outgoing longwave radiation (OLR) in the far-infrared (FIR) at high spectral resolution. The FIR spectral region is crucially important because it is responsible for over half of the Earth's emission to space. FORUM will capture the spectral window 100-1600 cm⁻¹, with water vapour (H₂O) the principal atmospheric absorber in the FIR region below 600 cm⁻¹. The aim of the FORUM mission

is to evaluate the role of the FIR in shaping the current climate, thereby reducing the uncertainty in predictions of future climate change which will prove crucial in future mitigation efforts.

The interpretation of measurements from FORUM is highly reliant on the ability to perform accurate radiative transfer calculations in the FIR region. Recent high-resolution measurements in the FIR have shown that there are deficiencies in the current HITRAN linelist. Here we report a new suite of high-resolution (up to 0.00096 cm⁻¹ spectral resolution) measurements of FIR spectra for pure and air-broadened H₂O, at temperatures in the range 240-296 K. These have been measured at synchrotron light source facilities (the Australian Synchrotron, Canadian Light Source and SOLEIL), which provide a more intense source of FIR electromagnetic radiation than a conventional laboratory, and using Bruker IFS 125HR spectrometers configured for the highest spectral resolutions.

We analyse spectra using the Labfit multispectrum fitting program, which has an extensive history in deriving non-Voigt line parameters for remote sensing. Through our analysis, we have derived new H₂O line parameters. These include line positions, line intensities, self- and air-broadened halfwidths, self- and air-pressure-induced shifts, along with temperature and speed dependence parameters. We compare our results to those from HITRAN database.

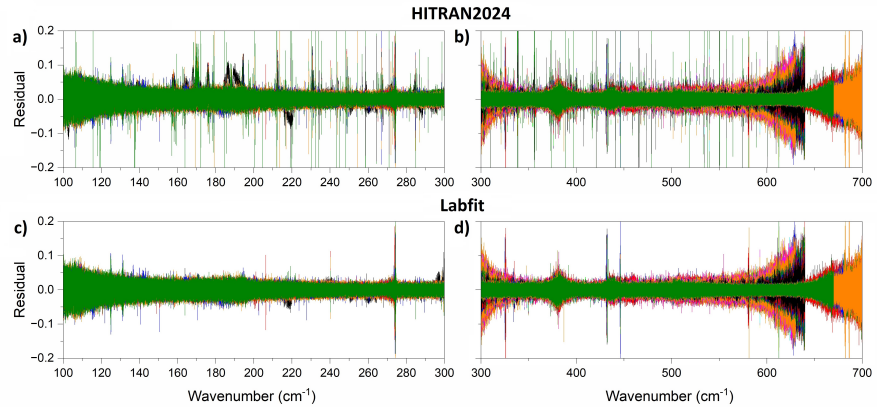


Figure 42: Residual spectra showing the subtraction of calculated from observed spectra for H₂O in the 100-700 cm⁻¹ region. For (a) and (b) the calculated spectra are derived from HITRAN2024 line parameters, and for (c) and (d) the calculated spectra are derived from the new Labfit line parameters. The remaining residuals in the Labfit-derived spectra are from synchrotron artefacts.

INVESTIGATION OF DARK-STATE PERTURBATIONS IN THE ν_{17} METHYL ROCKING BAND OF PROPYLENE OXIDE BY THE $2\nu_{22} + \nu_{24}$ AND $\nu_{20} + \nu_{24}$ COMBINATION BANDS

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Propylene oxide, the first chiral molecule identified in the interstellar medium, combines a rigid oxirane ring with a hindered methyl internal rotor and has long served as a model system for studying the interplay between methyl internal rotation and small-amplitude vibrations. The ν_{17} methyl rocking fundamental was recently reported to exhibit unexpectedly large A/E splittings, indicative of perturbative coupling to nearby torsionally excited dark states. In this work, we reanalyze this fundamental band using an expanded, multi-state framework. Using high-resolution laser spectroscopy and K_a -dependent diagnostic analysis of energy-level residuals, we identify $2\nu_{22} + \nu_{24}$ and $\nu_{20} + \nu_{24}$ as key combination bands playing a significant role in driving the anomalously large A/E splittings (up to 110 MHz) observed in the spectrum. Individual K-stacks were first fitted separately to diagnose the perturbation, after which a multi-state deperturbation fit in PGOPHER yielded the rotational constants of the dark states and the coupling constant W . Spectra were recorded using a continuous-wave ec-QCL (990 – 1060 cm^{-1} , 100 mW) in both a room-temperature glass cell and a 35 K supersonic jet with 42-pass Herriott-type absorption.

SPECTROSCOPIC LINE PARAMETERS OF CARBON DIOXIDE IN THE 500–850 cm^{-1} REGION

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Carbon dioxide (CO_2) is a strong absorber of infrared radiation. Its continuing increase within the Earth's atmosphere is a strong driver of climate change. The radiative forcing of climate associated with CO_2 occurs primarily within the wavenumber region 500–850 cm^{-1} . However, no current atmospheric sounder measures this entire CO_2 spectral signature at high spectral resolution; IASI, for example, cuts off at 645 cm^{-1} . The upcoming ESA FORUM (Far-infrared Outgoing Radiation Understanding and Monitoring) mission will measure the Earth's spectrally resolved outgoing longwave radiation (OLR) in the far-infrared at high-resolution for the first time, and cover this entire CO_2 region. In addition to the importance of this region for radiative forcing, the CO_2 features (above 650 cm^{-1}) are utilised for the retrieval of temperature profiles by meteorological satellites such as IASI and CrIS.

Here we report new high resolution (up to 0.00096 cm^{-1}) spectra of pure and air-broadened CO_2 at temperatures 200–296 K, measured using a Bruker IFS 125 HR spectrometer located at the Canadian Light Source. Line parameters have been extracted using the Labfit multispectrum fitting program, which has a history of deriving non-Voigt line parameters for remote sensing [1, 2]. Through our analysis, we are deriving line parameters including line positions, line intensities, self- and air-broadened halfwidths, self- and air-pressure induced shifts, temperature dependence parameters, and line mixing parameters using the full relaxation matrix approach. The results indicate some inaccuracies in the existing HITRAN line parameters [3].

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INSIGHTS INTO THE $\text{HNCO} \cdots \text{H}_2\text{O}_2$ COMPLEXES BY MATRIX ISOLATION INFRARED SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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This study presents the first integrated theoretical and experimental analysis of $\text{HNCO} \cdots \text{H}_2\text{O}_2$ complexes by matrix isolation infrared spectroscopy (MI-IR) and quantum-chemical calculations. The MI-IR technique allows the stabilization and precise vibrational characterization of reactive species or weakly bound complexes that are inaccessible in the gas phase at room temperature¹. In particular, complexation induces measurable shifts in vibrational frequencies, such as the redshifts observed in stretching modes involved in hydrogen bonding, thereby offering direct insight into intermolecular interactions^{2,3}.

Experiments were designed to obtain and spectroscopically characterize molecular complexes between HNCO (isocyanic acid) and H_2O_2 (hydrogen peroxide) under low-temperature matrix-isolation conditions. The method combined in situ generation of HNCO , controlled evaporation of H_2O_2 , co-deposition within an inert matrix (Ar and N_2), and infrared spectral acquisition by Fourier-Transform Infrared (FTIR) spectroscopy. The matrix was deposited at 15 K and the final spectra were measured at 10 K. The infrared spectra were measured using a Bruker 66 FTIR spectrometer equipped with a liquid-nitrogen-cooled HgCdTe detector. Spectra were collected in transmission mode with a spectral resolution of 0.5 cm^{-1} .

To support the assignment of the experimental spectra, the potential energy surfaces of the $\text{HNCO} \cdots \text{H}_2\text{O}_2$, $(\text{HNCO})_2 \cdots \text{H}_2\text{O}_2$, and $\text{HNCO} \cdots (\text{H}_2\text{O}_2)_2$ complexes were sampled using the CREST program⁴. The resulting clusters were first optimized at the B3LYP⁵ level of theory in conjunction with the 6-31+G*⁶ basis set and DFT-D3⁷ empirical dispersion (hereafter referred to as B3). The structures were subsequently refined using the double-hybrid rev-DSD-PBEP86-D3 functional⁸ with the 3F12⁻ basis set⁹ (all together denoted as rDSD). Thermochemical parameters were then obtained by performing anharmonic frequency calculations using the Hybrid Degeneracy-Corrected Vibrational Second-Order Perturbation Theory (HDCPT2)¹⁰ methodology at the B3 level. Relative populations were subsequently derived from Boltzmann distributions. Finally, anharmonic spectra were computed at the rDSD level using the Reduced-Dimensionality Generalized Vibrational Second-Order Perturbation Theory (RD-GVPT2) model¹¹. The comparison between theoretical and experimental spectra allowed the identification of the complexes formed in the experiments.

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HIGH RESOLUTION INFRARED, MICROWAVE AND MILLIMETER-WAVE SPECTROSCOPIES ON DIOXANE ISOMERS

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Dioxines are volatile organic compounds considered as atmospheric pollutants. Among them, 1,4-dioxane ($C_4H_8O_2$) is extensively released in the environment.[1] The spectroscopic detection and quantification of 1,4-dioxane in sub ppbv levels is still a challenge to analytical methods and generate concerns that 1,4-dioxane in the environment has mostly gone undetected. There is also a fundamental interest in monitoring these molecules in simulation chambers (CHARME at LPCA lab in Dunkirk) to study their reactivity with major oxidants but it requires knowledge of their rovibrational signatures through high-resolution experiments over a broad spectral range. We report here a high-resolution study of dioxane isomers on a wide infrared range (IR) combining the Jet-AILES set-up implemented at SOLEIL, and a room temperature long path cell, both coupled to a Fourier Transform Spectrometer (FTS), and the SPIRALES set-up available at MONARIS laboratory, a pulsed supersonic jet coupled to mid-IR quantum cascade lasers (QCL).[2] In the case of 1,4 dioxane, high resolution IR spectroscopy turns to be the best alternative to determine ground state molecular parameters in the absence of permanent dipole moment.[3] In the fingerprint region, several bands of 1,4-dioxane were analyzed using mainly both jet-cooled spectroscopic set-ups. Reliable ground and excited-state (ES) molecular parameters could be derived from global rovibrational fits distributed over 4 vibrational excited states including all possible projections of the vibrational dipole moment with different selection rules, which strongly reduces the correlations between molecular parameters. Last, a combined HR millimeter-wave, jet-cooled-QCL and cell-FT IR spectroscopic study of the very expensive 1,3 dioxane isomer enabled to derive precise molecular parameters for the ground state and 6 vibrational states in the 950-1250 cm^{-1} range. This present work focused about rovibrational analyses of dioxane isomers highlights the complementarity between supersonic jet set-ups and room temperature long path cells coupled to broadband FT and/or narrow band QCL infrared spectroscopies to characterize large molecules relevant for atmosphere science. [4]

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TRIPLE-RESONANCE SPECTROSCOPY USING A FREQUENCY COMB PROBE FOR HIGH-PRECISION MEASUREMENTS OF METHANE IN THE $12,000\text{ cm}^{-1}$ REGION

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Interpreting high-temperature spectra of methane from satellite- and ground-based observations requires accurate theoretical models verified by high-precision laboratory data. However, the scarcity of experimental data for levels above $10,000\text{ cm}^{-1}$ continues to hinder refinement of theoretical models. Here, we report an all-optical triple-resonance spectroscopy that links the ground state of methane to the C–H stretch band and its three overtones (i.e., $n\nu_3$ with $n = 1 - 4$, see Fig. 1a) and serves as a powerful tool

for investigating unexplored highly excited energy levels of methane up to $12,000\text{ cm}^{-1}$. A novel stepwise mid-infrared (MIR) pumping scheme is developed to populate a selected methane level in the $2\nu_3$ band. The pump fields are two idlers tunable around $3.3\text{ }\mu\text{m}$ produced by a double-pumped continuous-wave optical parametric oscillator, with their frequencies stabilized by referencing to an MIR frequency comb. In the proof-of-principle experiment, we populate the $(J, C) = (3, F_2)$ state in the $2\nu_3$ band by stepwise pumping the ν_3 Q(2, F_2) transition at 3018.65 cm^{-1} and the $2\nu_3 \leftarrow \nu_3$ R(2, F_1) transition at 3017.11 cm^{-1} . A cavity-enhanced frequency comb centered at $1.67\text{ }\mu\text{m}$ with a spectral span of 6 THz is used as a broadband optical probe to simultaneously detect tens of sub-Doppler transitions in the $3\nu_3 \leftarrow \nu_3$ and $4\nu_3 \leftarrow 2\nu_3$ ranges (see Fig. 1b). The probe spectrum is comb-mode-resolved by a home-built Fourier transform spectrometer and interleaved to a 2 MHz sample point spacing. Theoretical predictions from an effective Hamiltonian approach [1] and from ExoMol [2] are sufficiently accurate to allow unambiguous assignments in the $3\nu_3 \leftarrow \nu_3$ range. However, for the transitions in the $4\nu_3 \leftarrow 2\nu_3$ range, reaching levels in the $11900\text{--}12140\text{ cm}^{-1}$ region, the only available predictions from ExoMol are offset from the experiment by $>1\text{ cm}^{-1}$, which prevents firm assignments. This underlines the need for further studies in this spectral range. In future work, we will employ so-called combination-difference analysis [3] to rotationally assign the final states of the $4\nu_3 \leftarrow 2\nu_3$ transitions, which should enable full assignments using the ExoMol line list, and contribute valuable data to refine the prediction model of high-temperature spectroscopy.

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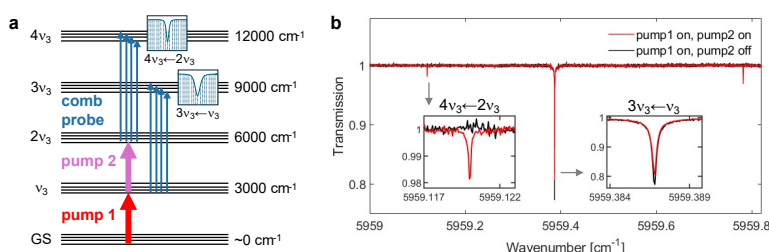


Figure 43: (a) Schematic of methane vibrational bands linked by the triple-resonance scheme. (b) Narrow section of probe spectra detected under two pump conditions; insets show a $4\nu_3 \leftarrow 2\nu_3$ transition and a $3\nu_3 \leftarrow \nu_3$ transition.

VUV-FT SPECTROSCOPY OF THE CAMERON SYSTEM ($a^3\Pi-X^1\Sigma^+$) AND DEPERTURBATION ANALYSIS OF THE $a^3\Pi$ ($\nu = 4$) STATE OF $^{12}\text{C}^{16}\text{O}$

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Carbon monoxide (CO) is one of the key molecules in astrophysical spectroscopy, where precise data on its energy level structure are essential for modelling the spectra of planetary and exoplanetary atmospheres. The Cameron system ($a^3\Pi-X^1\Sigma^+$) constitutes an important transition system in the vacuum ultraviolet (VUV) region, widely used, among others, in the analysis of atmospheric emissions of Mars and Venus [1–5].

In this work, a high-resolution absorption spectrum was recorded for the $\nu' = 4$ vibronic level of the Cameron $^{12}\text{C}^{16}\text{O}$ system using vacuum ultraviolet Fourier transform spectroscopy (VUV-FT) at the DESIRS beamline of the SOLEIL synchrotron [6]. A total of 191 spectral lines, comprising 9 branches, were identified. The wavenumbers of the spectral lines were determined to an accuracy of 0.01 cm^{-1} . The energy terms for the transition under study were also determined.

The rovibronic structure of the $a^3\Pi$ state ($\nu = 4$) was analysed using an effective Hamiltonian approach implemented in the PGOPHER program [7]. For each vibrational level, a set of 9 molecular constants was determined, describing the level energies, molecular rotation, and intrastate spin–orbit, spin–rotation, spin–spin coupling, as well as Λ -doubling phenomena.

For the $a^3\Pi(\nu = 4)$ level, deviations from regular behaviour were observed and described by determining perturbation parameters. The analysis showed that the observed irregularities arise from interaction with the $a'^3\Sigma^+$ state and significantly affect the structure of $a^3\Pi$.

The obtained molecular parameters, together with highly accurate experimental wavenumbers, represent a significant extension of the available spectroscopic data for CO and can be directly implemented in databases (e.g., ExoMol) as well as in VUV spectral modelling.

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COLLISIONAL LINE BROADENINGS AND SHIFTS IN THE S(0), S(1) AND S(2) ROTATIONAL RAMAN LINES OF HD IN AN H₂ BATH: EXPERIMENTAL MEASUREMENTS AND THEORETICAL CALCULATIONS

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We present a comparison between experimental and calculated collisional broadening and shift coefficients for the S(0), S(1), and S(2) pure rotational lines in the Raman spectrum of HD perturbed by collisions with H₂. The measurements were performed using stimulated Raman spectroscopy, whereas the calculations were carried out within a quantum close-coupling scattering formalism.

The stimulated Raman spectrometer uses a high-resolution, quasi-continuous-wave (q-CW) configuration combining one CW beam and one pulsed beam. The CW beam is generated by a dye laser operating at 17600.000 cm⁻¹ and frequency-locked using the readout of a high-resolution wavemeter, resulting in residual frequency jitter below 1 MHz. The tunable pulsed beam is generated by optically amplifying a CW seed in a pulsed dye amplifier pumped by the 532 nm output of a seeded Nd:YAG laser. The overall apparatus function is dominated by the spectral width of these tunable pulses and has a slightly asymmetric profile with a full width at half maximum (FWHM) of approximately 70 MHz, which determines the spectrometer resolution.

HD–H₂ mixtures containing 0.5–3% HD were prepared. Spectra of the S(0) and S(1) Raman lines were recorded at three temperatures—77, 195, and 298 K—whereas spectra of the S(2) line were recorded only at 195 and 298 K. At each temperature, spectra of each line were systematically registered at seven total pressures ranging from 25 to 800 mbar. Each line profile was fitted with a synthetic profile obtained by convolving the numerically determined apparatus function with a modified Hartmann–Tran (mHT) profile. Because the signal-to-noise ratio was insufficient to resolve the subtle speed-dependent effects, the corresponding mHT parameters were fixed at zero. Optimization of the remaining free parameters yielded the collisional widths, Γ , and shifts, Δ , of the measured lines. The collisional broadening coefficient, γ , and shift coefficient, δ , were obtained from linear regressions of Γ and Δ , respectively, as functions of pressure.

Quantum close-coupling scattering calculations were performed using our in-house BIGOS suite to compute the scattering S -matrices and corresponding generalized spectroscopic cross sections, σ_{λ}^q , based on a highly accurate six-dimensional *ab initio* potential energy surface for the HD–H₂ system.

1

The line-shape parameters were subsequently extracted from these quantities in a separate post-processing step. For the S(0), S(1), and S(2) lines, this procedure yielded the collisional broadening and shift coefficients, their speed dependences, and the complex Dicke parameters for the relevant rotational states of para- and ortho-H₂. Maxwell–Boltzmann averaging over collision energies, followed by averaging over the thermal H₂ rotational populations, provided the temperature dependences of these parameters. Reasonable agreement of the calculated broadening and shift coefficients with those retrieved from the stimulated Raman spectra provides a direct experimental test of the *ab initio* potential and the molecule–molecule scattering treatment.

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ROVIBRATIONAL SPECTROSCOPY OF HNCO^+ : A POTENTIAL PRECURSOR OF HNCO IN SPACE

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Isocyanic acid, HNCO , is ubiquitous in interstellar space having been detected in a wide variety of astronomical objects including, but not limited to high-mass star forming regions like Sgr B2,¹ translucent clouds² and external galaxies.³ Its formation chemistry, however, remains poorly understood. One potential gas-phase mechanism is the stepwise hydrogenation of NCO^+ to H_2NCO^+ followed by dissociative recombination leading to HNCO .⁴

The intermediate H_2NCO^+ has already been detected in space,⁵ motivating us to obtain laboratory spectroscopic data for HNCO^+ aiding its astronomical detection. Guided by broadband IR spectroscopy using the FELion cryogenic ion trap setup at HFML-FELIX,⁶ we measured the rovibrationally resolved spectrum of its H-N stretching mode near 3244 cm^{-1} using Leak-out spectroscopy⁷ at 19K and Ne as the collision partner. The experiments were carried out in the cryogenic 22-pole ion trap LIRtrap in Cologne.⁸ Tunable Infrared radiation was provided by a narrow linewidth (10^{-4} cm^{-1}) continuous-wave optical parametric oscillator.

The observed rotational substructure is consistent with an a-type rovibrational band of the N-H stretching mode of the nearly prolate asymmetric rotor $\text{HNCO}^+(X^2A'')$. Transitions with $K'_a = K''_a = 0$ were assigned and fitted using an effective Hamiltonian implemented in PGOPHER,⁹ with B' , C' , B'' and C'' included in the fit. In contrast, transitions with $K'_a = K''_a = 1$ appear strongly perturbed and no regular series could yet be assigned. These perturbations may be associated with the quasilinear nature of the molecule and contributions by the Renner-Teller effect. The assigned $K_a = 0$ transitions provide experimental constraints on the low- K_a rotational structure of HNCO^+ and constitute a first step toward reliable predictions of its pure rotational spectrum.

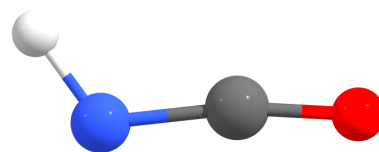


Figure 44: Equilibrium geometry of HNCO^+ calculated using CCSD(T)/cc-pCVTZ.

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AN IMPROVED STUDY OF CYANOACETYLENE AND DIACETYLENE INCLUDING THE STRONG $2\nu_5$ BAND OF HC_3N AND ν_4 BAND OF HC_4H

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Cyanoacetylene (HC_3N) and diacetylene (HC_4H) are key carbon-chain molecules in astrochemistry and planetary atmospheres. Reliable spectroscopic models of their infrared spectra are essential for astronomical observations, yet some of their strongest vibrational bands remain difficult to reproduce because of extensive anharmonic interactions. In this contribution, we present an improved high-resolution spectroscopic investigation of the HC_3N $2\nu_5$ overtone and the HC_4H ν_4 fundamental bands, combining synchrotron-based Fourier-transform infrared spectroscopy with complementary millimeter- and submillimeter-wave measurements. For HC_3N , a comprehensive global analysis of rotational and ro-vibrational transitions allowed us to characterize the complex resonance polyad involving the $v_5 = 2$, ($v_4 = 1, v_7 = 2$), ($v_6 = 2, v = 2$), ($v_5 = 1, v_7 = 3$), and $v_7 = 6$ vibrational states. The resulting effective Hamiltonian accurately reproduces more than 5300 experimental transitions and provides an improved description of the vibrational manifold up to about 1300 cm^{-1} . For HC_4H , the explicit treatment of the anharmonic interactions affecting the ν_4 C–H stretching band enabled the assignment of transitions up to $J = 115$ and significantly extended the characterization of this important infrared feature (Figure 1). The refined spectroscopic parameters and line lists have been incorporated into the HITRAN database, extending its coverage for both species and providing more reliable molecular data for the interpretation of high-resolution astronomical infrared observations.

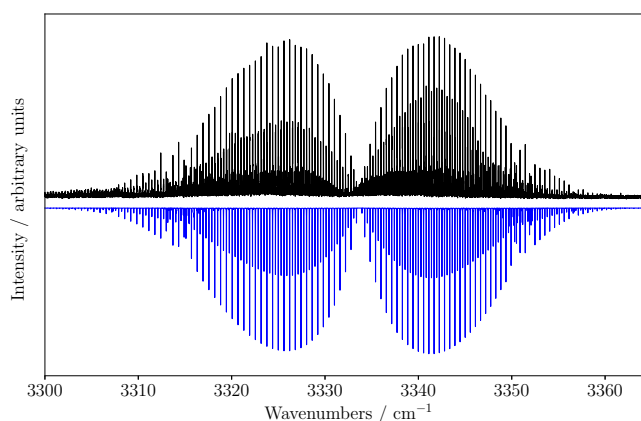


Figure 45: Recording (black trace) of the ν_4 band of HC_4H , together with a simulated spectrum (blue trace, reversed).

GLOBAL ANALYSIS OF METHYL INTERNAL ROTATION AND EXACT NUCLEAR QUADRUPOLE COUPLING IN 2-CHLOROPROPENE

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The simultaneous treatment of methyl internal rotation and nuclear quadrupole coupling is a challenging problem in rotational spectroscopy. 2-Chloropropene is a particularly suitable system for such investigations, featuring both a methyl group undergoing internal rotation and a chlorine atom. The methyl internal rotation splits each rotational transition into an A and an E torsional species. Since the torsional barrier is high, the internal rotation effect can be treated accurately with established Hamiltonian models. The chlorine nucleus further splits each torsional component into hyperfine transitions through its nuclear quadrupole coupling. With a nuclear spin of $I = 3/2$, the quadrupole interaction is sufficiently large that perturbative treatments become inadequate, while remaining considerably less pronounced than, for example, in bromine- or iodine-containing molecules.

2-Chloropropene was first investigated in 1965 by Unland, Weiss, and Flygare.¹ The vibrational ground and first excited states were analyzed, yielding the methyl torsional barrier as well as the chlorine nuclear quadrupole coupling constants. Although the rotational spectrum has subsequently been reinvestigated several times, internal rotation and nuclear quadrupole coupling effects have always been treated separately.^{2 3 4} In the present work, we recorded the microwave spectrum of 2-chloropropene between 2 GHz and 40 GHz using two resonator-based Fourier-Transform MicroWave (FTMW) spectrometers, the “big cavity”⁵ and the “small cavity”,⁶ thereby extending the frequency range covered by previous studies. Additional broadband survey spectra between 6 GHz and 20 GHz were recorded using the chirp-excitation mode of the PARIS (Passage And Resonance In Synergy) FTMW spectrometer.⁷ By employing a new version of the XIAM program,⁸ XIAM-NQ,⁹ which includes an exact treatment of the chlorine nuclear quadrupole coupling, global fits including the methyl internal rotation and nuclear quadrupole coupling effects were achieved for both the ³⁵Cl and ³⁷Cl isotopologues, with standard deviations within the measurement accuracy of 2 kHz.

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HIGH-RESOLUTION STUDY OF THE ν_{10} AND ν_9 BANDS OF ALLENE AROUND 11 μM

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Allene (propadiene, C_3H_4) and its isomer, propyne, were detected in Titan's atmosphere [1, 2]. The precise determination of their abundances is crucial to fuel chemical models of Titan's atmosphere. Indeed, the abundance of atomic hydrogen could be inferred from the ratio of the abundances of these two species [3]. To measure the abundances of allene and propyne, and investigate their seasonal and spatial variations, high resolution infrared spectra from ground- and space-based instruments are available. However, interpreting these observations relies on the availability of spectroscopic data for both molecules.

The present work aims at improving the description of line positions and intensities in the strong ν_{10} and ν_9 bands of allene, located respectively near 841 and 999 cm^{-1} . To do so, high resolution spectra of pure allene at room temperature and various pressures were recorded between 600 and 1200 cm^{-1} using a Bruker IFS 120 to 125 HR upgrade Fourier transform spectrometer. An effective Hamiltonian model was developed based on previous work [4] to reproduce the experimental spectrum. It enabled the identification of more than 5800 transitions in the recorded spectra. The spectroscopic constants used in the effective Hamiltonian are currently being refined to model the spectrum within experimental precision. The results of this ongoing study will be presented.

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HIGH-RESOLUTION SPECTROSCOPY AND MULTICHANNEL QUANTUM-DEFECT-THEORY ANALYSIS OF HIGH S AND D RYDBERG SERIES OF YTTERBIUM

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Highly excited Rydberg states of atoms with open-shell ion cores are interesting because of their potential in quantum-information-processing, quantum-sensing applications, and the determination of atomic properties. High-resolution spectroscopy is essential for characterising the electronic structure and dynamics of these atomic systems, in particular their photoionisation dynamics, their ionization energies, hyperfine structure and isotopic shifts. Ytterbium Rydberg states are particularly attractive in this context[1]. Previous studies of the Rydberg states of Yb have enabled the characterisation of the main triplet ($S=1$) series and the derivation of multichannel quantum-defect-theory (MQDT) models of increasing complexity [1-3]. However, several aspects remain insufficiently characterised. For instance, the spectra of ^{173}Yb Rydberg states are unknown and the MQDT analysis reported so far are isotopic specific and do not include perturbations in a systematic manner.

We present high-resolution spectra of the ns and nd Rydberg series of the $^{170}\text{Yb}(I=0, 3.05\%)$, $^{171}\text{Yb}(I=1/2, 14.30\%)$, $^{172}\text{Yb}(I=0, 21.90\%)$, $^{173}\text{Yb}(I=5/2, 16.12\%)$, $^{174}\text{Yb}(I=0, 31.80\%)$, $^{176}\text{Yb}(I=0, 12.70\%)$ recorded from the $[\text{Xe}]4f^{14}6s6p\ ^3P_2$ metastable state to the region below the $[\text{Xe}]4f^{14}6s\ ^2S_{1/2}$ ground ionic states. The experiments were carried out using a pulsed frequency-comb-calibrated Fourier-transform-limited narrow-band long-pulse UV laser and a supersonic-beam apparatus coupled to an ablation source of metastable Yb[4].

The new spectra reported in this contribution enabled a global MQDT analysis which (i) includes all isotopes with the same quantum-defect parameters, (ii) treats the hyperfine structure of ^{171}Yb and ^{173}Yb with a consistent set of parameters and (iii) systematically includes interactions with Rydberg states of low principal quantum number belonging to series converging to excited ion-core states with configurations $4f^{14}6snp$, $4f^{13}5d6snp$, $4f^{14}6pnp$. This analysis led to the derivation of an improved MQDT model which accurately describes the even-parity states of Yb. An improved value of the ionisation energy of the metastable Yb and the hyperfine structure of $^{173}\text{Yb}^+$ are determined.

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INFRARED SIGNATURES OF REFRACTORY MOLECULES: FROM LABORATORY SPECTROSCOPY TO MIRA STARS

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Refractory molecules are low-volatility species that remain stable at high temperatures. Here, we focus on oxygen-containing diatomic and triatomic molecules. Despite their small size, their gas-phase infrared spectra can exhibit considerable complexity due to hyperfine interactions, open-shell electronic states, and hot-band structure. The latter arises because vibrational cooling in a supersonic expansion is often less efficient than rotational cooling. The molecules are generated by laser ablation and characterized by infrared absorption spectroscopy, providing molecular parameters for comparison with astronomical observations.

As an astrophysical application, the laboratory results are compared with spectra of Mira variable stars obtained with NASA's Infrared Telescope Facility (IRTF). This enables molecular features to be assigned and their variation over the stellar pulsation cycle to be investigated. The work demonstrates how detailed laboratory spectroscopy provides the reference data required to identify refractory molecules in complex infrared environments.

FREQUENCY-MODULATED 200 GHz ROTATIONAL SPECTROSCOPY OF STYRENE OXIDE

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Styrene oxide ($\text{C}_8\text{H}_8\text{O}$) is a chiral molecule with three non-zero dipole moment components ($\mu_a = 0.6 \text{ D}$, $\mu_b = 1.0 \text{ D}$, $\mu_c = 1.3 \text{ D}$) making it a candidate for enantiomer-specific three-wave mixing experiments and a target for interstellar searches of aromatic chiral molecules. Its rotational spectrum was previously characterized over the range 2-330 GHz by Stahl et al. [1], providing spectroscopic constants. However, the 220-260 GHz region remains unexplored. We report measurements of the rotational spectrum of styrene oxide in this region using the frequency-modulated 200 GHz absorption spectrometer. Continuous-wave radiation in the 220-260 GHz range was generated by a frequency multiplied microwave synthesizer and the spectrum was recorded at room temperature with phase sensitive 2f detection employing a lock-in amplifier. The recorded spectrum shows the characteristic near-prolate asymmetric rotor structure dominated by rQ_{Ka^-} branch clusters and a dense R-branch background. Observed line positions are in good agreement with predictions based on the Watson A-reduction Hamiltonian constants of Stahl et al. [1]. In addition to rotational transitions of ground vibrational state, numerous spectral features were observed that are attributed to low-lying vibrationally excited states populated at room temperature. The new measurements extend the available spectroscopic database for this molecule. These measurements provide a basis for future investigations of vibrationally excited states and chirality-sensitive microwave spectroscopy.

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ROTATIONAL SPECTRA OF FOUR CONFORMERS OF ALLYLAMINE

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Recent astronomical detections in the interstellar medium of several molecules containing an amino functional group – including hydroxylamine[1], vinylamine[2], *syn*-glycolamide[3], and methyl carbamate[4] – demonstrate that a diverse array of NH₂-bearing species can form and persist under harsh interstellar conditions. In this context, allylamine (CH₂=CHCH₂NH₂) represents a promising candidate for future interstellar searches. Allylamine exists in five stable conformations[5-6] arising from rotation about its C-C and C-N bonds. In this work, we report the analysis of the room-temperature rotational spectrum of allylamine recorded up to 320 GHz. Rotational transitions corresponding to the ground vibrational state, as well as several low-lying vibrationally excited states, have been assigned for the four most stable conformers. The spectra were analyzed by means of a semirigid rotational Hamiltonian, and the large-amplitude amino inversion motion was investigated. This work significantly extends previous microwave studies[7-10], providing refined rotational constants and previously undetermined centrifugal distortion constants to generate comprehensive and accurate spectral line catalogs to guide radio astronomical searches.

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TEMPERATURE-DEPENDENT PHOTODISSOCIATION CROSS SECTIONS AND RATES FOR NH AND H₂S

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Molecular photodissociation impacts the composition and dynamics of many terrestrial and astronomical environments. The vacuum ultraviolet irradiation of an exoplanet by its host star, for instance, leads to complex photochemistry in its upper atmosphere that drives the system away from equilibrium. In the study of exoplanets and other hot astronomical bodies, it is thus critical to understand the effect of temperature on such processes. Accordingly, this work presents temperature-dependent photodissociation cross sections and rates for both imidogen (NH) and hydrogen sulphide (H₂S). The latter is of particular importance in light of recent SO₂ detections using the James Webb Space Telescope [1]. The theoretical approach employed in this study relied on a time-independent variational framework with exact kinetic energy operators.

For NH, a new spectroscopic model was assembled for the lowest 12 electronic states. This model was utilised to compute bound-bound line lists for all isotopologues using the diatomic nuclear motion program Duo [2]. For the main isotopologue, temperature-dependent photodissociation cross sections, including both direct and predissociative contributions, and rates were calculated. These data cover all spectral features with wavelengths longwards of the hydrogen Ly α line and molecular temperatures up to 10 000 K. The rates are shown to increase by several orders of magnitude with molecular temperature under cool stellar radiation fields. The predissociative lifetimes of quasi-bound states were determined using the stabilisation approach [3].

For H₂S, the first electronic absorption band was studied using *ab initio* potential energy, coupling, and transition dipole moment surfaces in both the adiabatic and diabatic representations. The spectral calculations required updates to the triatomic nuclear motion program EVEREST [4], which now allows for diabatically-coupled states to be treated within the time-independent variational framework. It is shown that the inclusion of non-adiabatic effects, associated with conical intersections between the excited 1 ¹A₂ and 1 ¹B₁ electronic states, is essential to model the low-energy wing of the spectrum in the near-threshold region.

The study of these two molecules together highlights the need for temperature-dependent ultraviolet data for photochemical and radiative transfer applications. All cross sections reported in this work are compared to experimental measurements where available. The photodissociation rates are computed for important radiation fields, including interstellar and black-body fluxes.

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ROVIBRATIONAL POPULATION REDISTRIBUTION IN JET-COOLED N₂O PROBED BY IR–MILLIMETER-WAVE DOUBLE RESONANCE

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We investigate rovibrational excitation and collision-induced population redistribution in supersonic jets, using N₂O as a test system. Selected rovibrational states are excited with a narrow-linewidth continuous-wave optical parametric oscillator, and their populations are probed via the $J = 4 \leftarrow 3$ rotational transition near 100 GHz, using chirped-pulse millimeter-wave excitation and detection of the resulting free-induction decay (FID).

The FID amplitude is studied as a function of stagnation pressure, distance from the nozzle, and nozzle geometry. A Mach-number-based description of the expansion relates these experimental parameters to the local pressure, temperature, and number density. The observed signal reflects the competing effects of increasing molecular density, collision-induced population redistribution, and loss of coherence. Pinhole and slit nozzles are used to compare nominally three-dimensional and two-dimensional expansions, and to determine the jet conditions that maximize the state-selective signal.

Population redistribution is investigated further following excitation of different rovibrational transitions. Because the $J = 4 \leftarrow 3$ probe transition shifts for each vibrational satellite, the initially prepared state and lower-lying states populated by collisions can be distinguished in the millimeter-wave spectrum. Excitation of the 10^01 state reveals preferential transfer to 10^00 and, to a lesser extent, 00^01 , while selective excitation of the e - and f -parity components of 01^11 allows collision-induced parity redistribution to be probed.

OFF-AXIS CAVITY RING-DOWN SPECTROSCOPY OF JET-COOLED MOLECULES AT 3 μM

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We present the development of a high-resolution cavity ring-down spectrometer from on-axis to off-axis operation. The setup employs a cw optical parametric oscillator (OPO) covering 2.7–4.0 μm and a 0.3 m high-finesse cavity with a measured mirror reflectivity of 99.983 % (finesse 1.8×10^4 , ring-down time 5.8 μs). In conventional on-axis operation, the occurrence of cavity resonances is subject to timing jitter. While this is uncritical for many spectroscopic measurements, deterministic timing is required for processes on the microsecond scale, such as the approximately 10 μs transit of laser-ablated molecules through the cavity mode or synchronized millimeter-wave chirped-pulse excitation.

Following Chu et al. [1], off-axis coupling [2] is combined with white-noise linewidth broadening using an electro-optic modulator, providing quasi-continuous cavity transmission. In contrast to their diode-laser implementation, we broaden the OPO pump, so that the modulation is transferred to the idler and the scheme becomes available over the full OPO tuning range. An acousto-optic modulator initiates the ring-down event at a selected time, while a Herriott-type multipass reinjection mirror [3] improves the utilization of the light incident to the ringdown cavity, resulting in increased transmission. Characterization on the Q branch of the $(13^10) \leftarrow (00^00)$ band of N_2O near 3046.2 cm^{-1} yields a noise-equivalent absorption of $4.7 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$, with the band head detected at a signal-to-noise ratio of 16 in a single 33 ms jet shot at a jet repetition rate of 30 Hz. High-resolution measurements of jet-cooled styrene oxide are in preparation; laser-ablated carbon chains and metal hydrides are planned for the future.

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BENCHMARKING EDOT: PRECISE STRUCTURAL DETERMINATION OF THE MONOMER AND ITS WATER CLUSTER BY JET-COOLED ROTATIONAL SPECTROSCOPY

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This work presents an experimental investigation of 3,4-ethylenedioxythiophene (EDOT), a key building block for polythiophenes, a class of conjugated polymers¹ renowned for their excellent conductive properties. Since their discovery in the 1980s, polythiophenes, particularly in their doped forms, have found widespread applications in electronics,² from antistatic coatings and capacitors to organic light-emitting diodes (OLEDs) and solar cells,³ and more recently in bioelectronic medicine.⁴ Despite this technological relevance, the geometrical properties of the EDOT monomer remain completely unexplored experimentally. This study fills that gap by providing the first high-resolution rotational spectroscopy characterization of the monomer, a fundamental prerequisite for the accurate parametrization of computational models used to simulate larger polymeric systems. The rotational spectrum of EDOT was recorded under jet-cooled conditions in a supersonic expansion using the free-jet absorption millimeters wave and the pulsed-jet Fourier transform microwave spectrometers at the University of Bologna.

Furthermore, the assignment of singly substituted ¹³C, ³⁴S, and ¹⁸O isotopologues in natural abundance allowed for a complete structural elucidation. The empirically derived spectroscopic parameters provide a rigorous benchmark for theoretical methods and are crucial for understanding the monomer's structural and electronic features that underpin its function as a precursor for piezochromic copolymers.

In a complementary effort, molecular clusters of EDOT with a single water molecule were also investigated. A conformational search software identified several low-energy minima, which were subsequently optimized. To date, the rotational spectrum of the global minimum of the monohydrated cluster has been successfully assigned.

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COMPACT LASER ABLATION SOURCE SYSTEM FOR HIGH-RESOLUTION MOLECULAR SPECTROSCOPY

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Small refractory molecules are important constituents of the circumstellar envelopes of late-type stars and contribute to their infrared and submillimeter spectra. High-resolution laboratory spectroscopy is required to identify these species and support their quantification in astronomical observations. Many of these species are radicals, highly reactive, or difficult to maintain in the gas phase at sufficient concentrations. They must therefore be generated and probed in situ.

Laser ablation sources are widely used to produce pulsed supersonic jets containing refractory species. In our laboratory, a laser ablation source with frontal UV laser light input has enabled studies of astrophysically relevant molecules such as Si₂C, Al₂O, TiO, AlO, VO, FeO, and others, including submillimeter measurements. However, future sensitive measurements using an off-axis cavity ring-down spectrometer require a more compact and mechanically reliable design.

As part of a master's thesis project, we present a redesigned laser ablation source that reduces the footprint while maintaining continuous sample-rod rotation and translation to expose fresh target material. Key changes include compact drive components, flexible couplings, improved bearing-cap sealing, and bidirectional control with limit-switch protection. The resulting system provides a smaller, more robust, and vacuum-compatible platform for next-generation high-resolution spectroscopy of refractory molecules.

MICROWAVE SPECTRA OF 2-CHLORO-3-METHYLTHIOPHENE AND 2-CHLORO-5-METHYLTHIOPHENE: LOW-BARRIER METHYL INTERNAL ROTATION AND EXACT TREATMENT OF CHLORINE NUCLEAR QUADRUPOLE COUPLING

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Low-barrier methyl internal rotation has attracted considerable attention in substituted thiophenes over the past decade.¹ Introducing a chlorine substituent adds a second quantum mechanical effect, namely nuclear quadrupole coupling, whose simultaneous treatment with internal rotation remains challenging. Because only a few chlorinated molecules exhibiting low-barrier methyl internal rotation have been investigated to date, 2-chloro-3-methylthiophene and 2-chloro-5-methylthiophene provide ideal benchmark systems for investigating how the position of a chlorine substituent modifies the methyl torsional barrier.

We report the rotational spectra of 2-chloro-3-methylthiophene and 2-chloro-5-methylthiophene recorded between 2 and 26.5 GHz using a molecular jet, cavity-based Fourier-transform microwave spectrometer called „the big cavity".² The spectra of both the ³⁵Cl and ³⁷Cl isotopologues were assigned, including A-E torsional splittings arising from the internal rotation of the methyl group. Separate fits of the A and E torsional species were performed with the program *SPFIT*.³ To account simultaneously for methyl internal rotation and chlorine nuclear quadrupole coupling, the spectra were fitted using a modified version of the *XIAM* program⁴, *XIAM-NQ*⁵, which provides an exact treatment of the chlorine nuclear quadrupole interaction. The experimentally determined torsional barriers are in good agreement with results from MP2/6-311++G(d,p) calculations. For 2-chloro-5-methylthiophene, the barrier of 246 cm⁻¹ is consistent with those reported for related methylthiophene derivatives.^{6,7,8} In contrast, the barrier of 47 cm⁻¹ for 2-chloro-3-methylthiophene is remarkably low. Because the methyl and chlorine substituents occupy adjacent positions on the thiophene ring, a substantially higher barrier would be expected due to steric hindrance. The present results therefore provide further evidence that steric effects alone are insufficient to explain the torsional barrier associated with methyl internal rotation.

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¹³C- AND ¹⁵N-MONOSUBSTITUTED ISOTOPOLOGUES OF HC₃N: CHARACTERIZATION OF THE RESONANCE SYSTEMS

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We present a detailed investigation of the pure rotational spectra of four rare isotopologues of cyanoacetylene — H¹³CCCN, HC¹³CCN, HCC¹³CN, and HCCC¹⁵N — recorded between 75 and 530 GHz using a frequency-modulated millimeter-wave spectrometer. Over 4000 transitions were assigned in the $J = 9\text{--}58$ range, covering the ground and the $v_7 = 1\text{--}4$, $v_6 = 1\text{--}2$, $v_5 = 1$, $v_4 = 1$, $v_7 = v_5 = 1$, and $v_6 = 1 + v_7 = 1\text{--}2$ vibrationally excited states. Global fits including previous literature data ^{1 2 3} yielded state-effective spectroscopic constants, including rotational constants, centrifugal distortion constants,

anharmonic $x_{L(tt)}$ and $x_{L(tt')}$ constants, and ro-vibrational l -type term coefficients. Vibrational interactions were modeled explicitly: the $v_5 \sim v_7 = 3$ dyad and the $v_4 = 1 \sim v_5 = v_7 = 1 \sim v_6 = 2 \sim v_7 = 4$ polyad were analyzed, allowing for the identification of 15 previously unassigned inter-state transitions. High-level quantum-chemical calculations at the CCSD(T)/cc-pVQZ level were performed to support the analysis and to provide reliable estimates of the spectroscopic parameters not directly determinable from the fit. The resulting extended isotopic dataset will support the astrophysical modeling of cyanoacetylene in regions where HC₃N emission is optically thick.

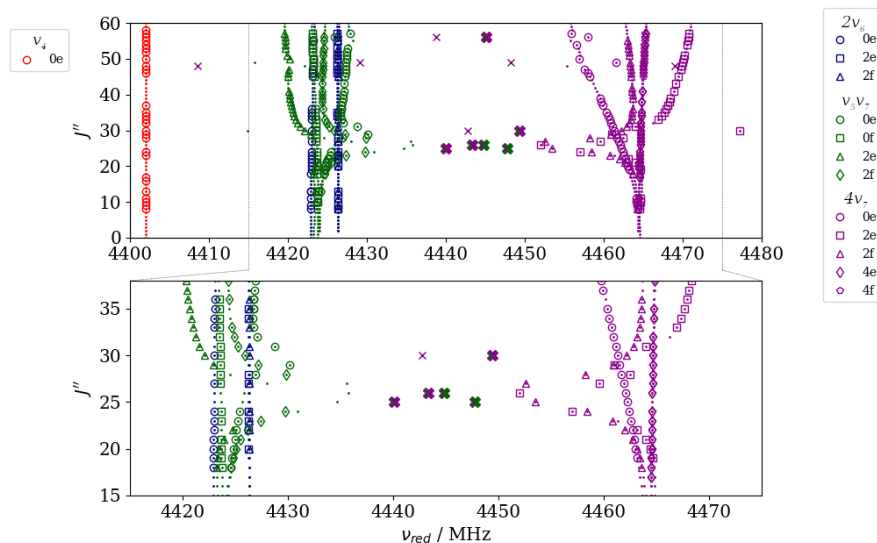


Figure 46: Reduced frequency diagram for the $v_4 = 1 \sim v_5 = v_7 = 1 \sim v_6 = 2 \sim v_7 = 4$ polyad of H¹³CCCN. Legends report the labeling of l -sublevels of each state. Dots indicate predicted line positions while solid symbols mark the measured lines. Interstate transitions at the avoided crossings are labeled with solid crosses.

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COMPARATIVE ROTATIONAL SPECTROSCOPIC STUDY OF HYDRATED CO₂ AND SO₂ MOLECULAR CLUSTERS

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Microsolvation provides an ideal framework for investigating the interplay between hydrogen bonding and weak intermolecular interactions in molecular aggregates. In this work, we present a comparative rotational spectroscopic study of hydrated carbon dioxide and sulfur dioxide clusters, revealing how the different electronic properties of CO₂ and SO₂ influence the structures adopted upon sequential aggregation with water.

We have characterized the rotational spectra of small CO₂ and SO₂ clusters in the presence of water under supersonic jet expansion conditions using chirped-pulse Fourier-transform microwave spectroscopy. The experimental results were analyzed in combination with quantum-chemical calculations, allowing the unambiguous structural assignment of the observed species.

For the CO₂ system, the structural series includes the previously characterized CO₂–H₂O [1], CO₂–(H₂O)₂ [2], and (CO₂)₂–H₂O [3] complexes, together with the newly identified (CO₂)₃–H₂O complex and their isotopologues. The corresponding SO₂ family comprises the previously reported (SO₂)₂ dimer [4] and SO₂–H₂O complex [5], whose spectroscopic characterization was extended through isotopic substitution and the measurement of additional rotational transitions, together with SO₂–(H₂O)₂ and SO₂–(H₂O)₄.

These complementary aggregation patterns reflect the different balance between intermolecular and hydrogen-bonding interactions dictated by the electronic properties of the nonpolar CO₂ molecule and its polar SO₂ analogue. Overall, this work provides new molecular-level insights into the mechanisms governing microsolvation and the formation of weakly bound atmospheric clusters, while establishing accurate structural benchmarks for future experimental and theoretical investigations.

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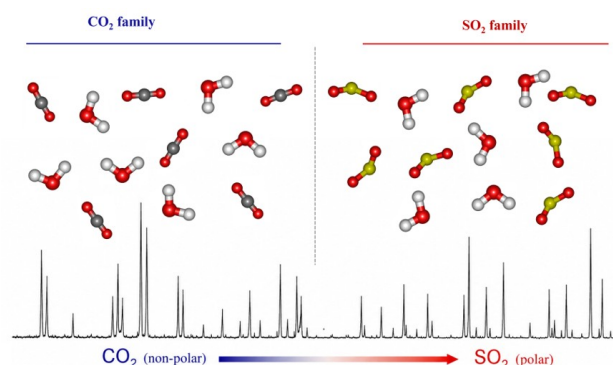


Figure 47: Microwave investigation of CO₂ and SO₂ hydrated clusters

THE HIGH RESOLUTION SPECTRUM OF THE ν_2 BAND OF THE ELUSIVE HSCO^+

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We have recorded the high resolution spectrum of the ν_2 band of the HSCO^+ cation using an infrared difference frequency spectrometer coupled to a hollow cathode discharge, in a conventional absorption experiment. A combination band ($\nu_2 + \nu_3$) has also been detected using the Leak-Out-Spectroscopy (LOS) technique in a cryogenic ion trap. Previous attempts to identify the IR spectrum of this ion in the S-H stretching region in the same experimental conditions that allowed the identification of HOCS^+ had been unsuccessful^{1,2}, although theoretical calculations³ predict the latter to be less stable by ~ 4.86 kcal/mol. Similarly, HSCO^+ has not been identified in space in the same region where HOCS^+ has been observed⁴.

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HIGH-RESOLUTION INFRARED SPECTROSCOPY OF N₂O BROADENED BY HE, AND H₂ TO ASSIST IN ANALYSIS OF EXOPLANETARY ATMOSPHERES.

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The James Webb Space Telescope (JWST), launched in 2021, together with upcoming facilities such as the Extremely Large Telescope (ELT), ARIEL, and GRAVITY+, is expected to deliver improved-resolution spectroscopic data of exoplanetary atmospheres across the optical to mid-IR range. These observations will improve our understanding of atmospheric composition through the retrieval of molecular abundances, and provide new insights into planetary formation and evolution (Tinetti et al., 2018). Interpretation of these spectra requires accurate line modeling based on high-resolution spectroscopy data from laboratories, including transition frequencies, line intensities, and temperature-dependent and pressure(P)-broadening coefficients. These parameters are compiled in databases such as HITRAN (Gordon et al., 2026, Tan et al., 2022) and ExoMol (Tennyson et al., 2024).

While these catalogs contain molecular line lists for spectral modeling, laboratory measurements are limited for many molecular parameters required to accurately determine molecular abundances in exoplanet atmospheres. For example, N₂O is a biosignature gas with distinctive spectral features in the near- and mid-IR range (Grenfell et al., 2014, Schwieterman et al., 2022). However, current laboratory studies of P-broadening of N₂O-He (Tasinato et al., 2010, Nakayama et al., 2007) are insufficient for deriving a reliable model and are therefore supplemented with N₂O-CO₂ broadening coefficients in HITRAN (Nakamichi et al., 2006). In the case of N₂O-H₂ P-broadening, very limited experimental data are available (French et al., 1968, Tubbs et al., 1973), preventing reliable extraction of broadening parameters and consequently limiting their inclusion in HITRAN.

To address this, we present high-resolution gas-phase spectroscopy of N₂O broadened by He and H₂ using a Bruker IFS 120/5HR Fourier-transform infrared spectrometer. We report our latest experimental results for the ν_3 fundamental band, the overtone ($2\nu_1$), and the combination band ($\nu_1 + 2\nu_2$) of N₂O broadened by He and H₂ at room temperature and pressures up to 1 bar. This work aims to provide laboratory data that support the inclusion of N₂O-H₂ and N₂O-He P-broadening parameters in HITRAN, enhance existing spectroscopic databases, and enable more accurate characterization of exoplanetary atmospheres.

LASER SPECTROSCOPY OF FeH: CHARACTERIZING THE MAGNETIC RESPONSE OF SELECT LEVELS IN THE $A^4\Pi$ STATE

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FeH is often observed in the atmosphere of cool M and L type stars. Its (0,0) $D^4\Pi$ - $A^4\Pi$ system near 1.65 μm (formerly called $E^4\Pi$ - $A^4\Pi$) is particularly intense and exhibits a strong magnetic response, making it a promising diagnostic tool. In 2004^a, astronomers found that the magnetic response could not be calculated assuming purely Hund's case (a) or (b) for either the $D^4\Pi$ or $A^4\Pi$ state and urged that laboratory and/or theoretical investigations were needed. In this work we used a tunable dye laser to probe select levels of the $A^4\Pi$ $v = 0$ state under magnetic field to characterize their magnetic response. We used transitions with newly discovered upper levels (to access the $A^4\Pi$ $v = 0$ state), which belong to upper state(s) that we have been unable to identify. As each upper level contacted several lower $A^4\Pi$ state levels, we implemented a global profile fitting technique to utilize the self-consistency to improve measurement accuracy.

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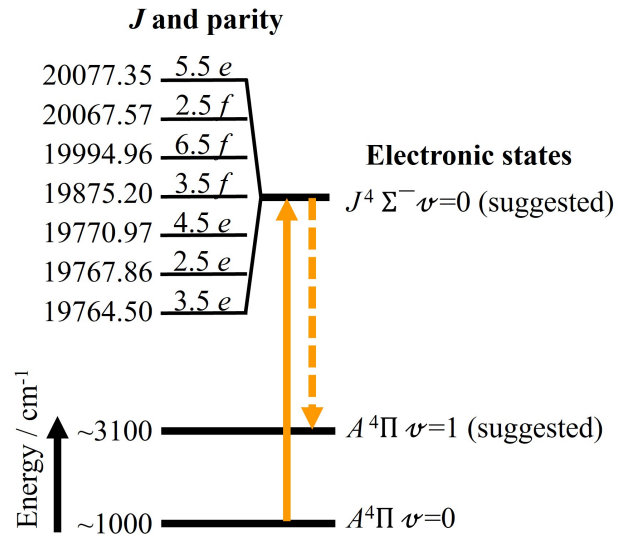


Figure 48: Outline of how we accessed $A^4\Pi$ $v = 0$ levels with direct laser excitation. We detected on transitions with lower levels we suggest belong to $A^4\Pi$ $v = 1$.

MOLECULAR-LEVEL INSIGHTS INTO CO₂ CAPTURE AND COMPETITIVE BINDING WITH WATER IN ORTHO-FLUOROANILINE: A ROTATIONAL STUDY

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Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are promising materials for CO₂ capture.[1] In this realm, understanding the intermolecular interactions that govern CO₂ adsorption and its competition with H₂O is essential for the design of improved capture systems.[2] Since these porous materials are assembled from cyclic molecular building blocks, ortho-fluoroaniline is a suitable template to study these systems since it combines a cyclic aromatic scaffold with an amino group, a common CO₂ adsorption site, while its fluorine substituent can elucidate the effect of fluorination on the balance of intermolecular interactions.[1]

Complexes formed between ortho-fluoroaniline, CO₂, and H₂O were created in supersonic jet conditions and measured with a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer operating in the 2–8 GHz frequency range. Complementary quantum chemical calculations were carried out using CREST for the conformational search, and ORCA at the DFT/B3LYP-D3BJ/def2-TZVP level of theory for posterior geometry optimizations. Ortho-fluoroaniline-CO₂ and ortho-fluoroaniline-H₂O complexes were observed, together with two distinct ortho-fluoroaniline-CO₂-H₂O ternary complexes.

Our results reveal that CO₂ binds to ortho-fluoroaniline through a tetrel C⋯N interaction between the carbon atom of CO₂ and the amino nitrogen, whereas H₂O binds to the same nitrogen through a hydrogen bond, demonstrating direct competition for the adsorption site (see Figure 1). The ternary complexes are consistent with sequential aggregation, where the first guest binds to the amino nitrogen, pushing the other away from its preferential docking site. In all complexes, the preferred binding geometry is located on the side opposite of the fluorine substituent, suggesting that fluorination does not participate directly in physical CO₂ adsorption. In contrast, the calculated binding and formation energies of fluorinated and non-fluorinated complexes differ appreciably, indicating that fluorination has a significant role on the energetic balance of intermolecular interactions, with a tendency to help the formation of complexes where CO₂ interacts directly with the amine, as opposed to complexes where water interacts directly with the amine. These results provide molecular-level insight into the role of fluorination in aromatic amine building blocks relevant to MOF- and COF-based carbon capture materials.

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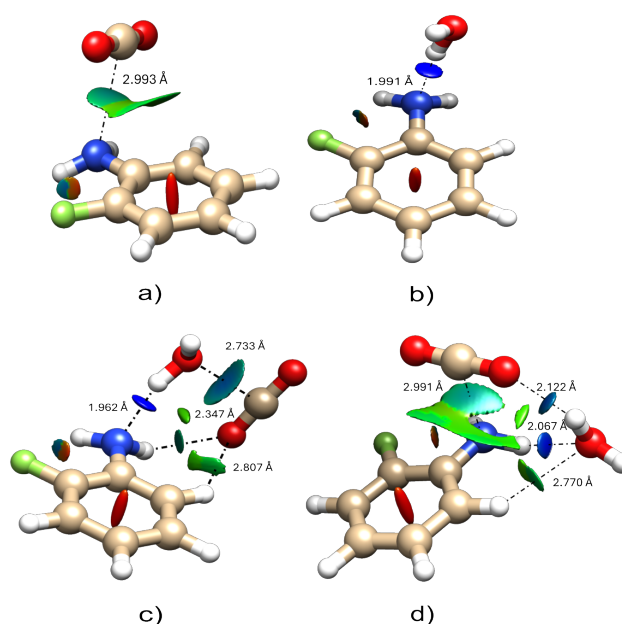


Figure 49: Molecular structures of a) ortho-fluoroaniline-CO₂, b) ortho-fluoroaniline-H₂O and two distinct c) and d) ortho-fluoroaniline-CO₂-H₂O complexes.

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AN *AB INITIO* ROVIBRATIONAL LINELIST FOR HPO

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HPO appears important as a key intermediate species for phosphine synthesis on Venus (Mráziková et al., *Astrobiology*, **24**(4), 407 (2024)) and is included in the modeling of 55 Cancri e (Zilinskas et al., *A&A*, **697**, A34 (2025)). Here we present the production of an *ab initio* rotation-vibration line list for the HPO molecule in its ground electronic state. The potential energy and dipole moment surfaces are computed using CCSD(T)-F12b with the cc-pVQZ-F12 and aug-cc-pV(5+d)Z basis sets, respectively, on a grid of 5000 geometries spanning energies up to 20000 cm⁻¹. Variational calculations performed using the nuclear motion program TROVE include total angular momentum states up to $J = 150$ with energies spanning up to 30,000 cm⁻¹ and transitions covering the wavenumber range up to 20,000 cm⁻¹. Fundamental vibrational frequencies are in good agreement with limited experimental and earlier theoretical values. This is the first comprehensive line list for HPO applicable for a large range of temperatures. It will be included in the ExoMol database.

PROBING THE SURFACE CHEMISTRY TOWARDS INTERSTELLAR DUST GRAINS: (SUB-)MILLIMETER-WAVE SPECTROSCOPIC CHARACTERIZATION OF NH_2Cl

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Under interstellar conditions, monochloramine (NH_2Cl) is believed to be formed by surface reactions between adsorbed nitrogen, hydrogen, and chlorine atoms. As such, it is considered an important probe for the mobility of nitrogen and a potential secondary reservoir of chlorine, along with HCl and CH_3Cl . Available laboratory data on this species do not cover the (sub-)millimeter-wave domain (> 60 GHz), where the strongest transitions lie, even at low temperature, preventing interstellar searches. In this context, a comprehensive pure rotational characterization of $\text{NH}_2^{35}\text{Cl}$ and $\text{NH}_2^{37}\text{Cl}$ has been carried out in this work. The experimental (sub-)millimeter-wave spectra of both isotopologues have been recorded in the Doppler regime between 75 and 880 GHz with a broadband chirped-pulse Fourier transform microwave spectrometer and a source-frequency-modulated (sub-)millimeter-wave spectrometer. In order to further improve the accuracy of the analysis, some lines have been recorded in the sub-Doppler regime by exploiting the saturation spectroscopy technique known as Lamb dip. More than 2200 distinct frequencies belonging to $\text{NH}_2^{35}\text{Cl}$ and more than 1000 of the less abundant isotopologue $\text{NH}_2^{37}\text{Cl}$ have been assigned, determining with high accuracy the spectroscopic constants. Notably, the inversion splitting due to the amino inversion motion is experimentally determined for the first time. An astronomical search for the main isotopologue ($\text{NH}_2^{35}\text{Cl}$) has been carried out toward the young protostar IRAS 16293–2422 through the high-resolution spectral survey COMPASS. No line could be unambiguously detected, but an upper limit on the column density has been derived and compared with predictions from our best model.

MACHINE LEARNING IN THE EXOMOL PROJECT

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Since 2011, the ExoMol database has been a vital resource to the astronomical community for modelling the spectral properties of hot atmospheres, including those of exoplanets, brown dwarfs, and cool stars. Providing comprehensive molecular line lists, ExoMol currently hosts over 1 trillion transitions, across 100+ molecules and 250+ isotopologues. The sheer volume and complexity of this dataset present unique challenges and opportunities for the application of machine learning (ML) techniques.

A significant recent application of ML in ExoMol is the study of line broadening by Guest *et al.* (2024, 2026) [1, 2]. Accurate pressure broadening parameters are critical for interpreting atmospheric spectra but are often missing for the exotic species present in exoplanet atmospheres. A new model capable of predicting gamma for unseen molecule-perturber pairs is presented. This allows for the mass production of broadening data across the ExoMol database, filling critical gaps that traditional experimental or theoretical methods could not practically address.

Work has also commenced on increasing the accuracy of minor isotopologues in the database utilising neural networks by Barnfield *et al.* (2026) [3], which are essential for constraining the evolutionary history of planetary bodies through isotope ratios. Additionally, the focus shifts to the "big data" challenge of quantum number assignment.

With future work, molecular line lists can contain billions of transitions, too many to assign rigorous quantum number labels to by hand. We will develop machine learning models that treat each spectral line as a connection between two unknown energy levels. Energy conservation and selection rules then constrain which lines can share a level, the relations underlying the Ritz combination principle. Labelled levels can be tied to empirically determined energies, sharpening the line positions on which high-resolution cross-correlation spectroscopy depends, improving upon the line lists underpinning Ariel's atmospheric retrievals. This work forms a core strand of the UCL Centre for Doctoral Training in Data Intensive Science (DIS CDT) and ERC ExoMol grants.

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3,3,4,4,5,5,6,6,6-NONAFLUOROHEXAN-1-OL: A COMBINED ROTATIONAL SPECTROSCOPY AND QUANTUM-CHEMICAL STUDY OF A PARTIALLY FLUORINATED ALIPHATIC ALCOHOL

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Fluorinated alcohols are widely employed across the chemical, pharmaceutical and materials industries, and are now recognised as ubiquitous environmental contaminants. Their broad applicability stems from a distinctive set of physico-chemical properties, which ultimately originate from the peculiar pattern of intra- and intermolecular interactions that fluorination introduces into an otherwise ordinary alcohol framework. Rotational spectroscopy in supersonic expansion offers a direct route to probe how such interactions shape the conformational space of these systems at the isolated-molecule level.

Here we present a broadband CP-FTMW study of 3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (NFH) in the 2.0–6.5 GHz region. NFH is a partially fluorinated medium-chain aliphatic alcohol in which several competing effects contribute to shaping the conformational landscape. The conformational space has been characterized with ORCA 6.0, using Global Optimizer Algorithm (GOAT) for the initial sampling and CAM-B3LYP/def2-TZVP for structure refinement. Several monomer conformers have been assigned in the jet-cooled spectrum, and the analysis of the corresponding 1:1 water complex is currently in progress. In parallel, a statistical analysis has been performed on a homologous series of C6 fluoroalcohols at different degrees of fluorination to understand how fluorination of the carbon chain reshapes the conformational equilibria of the isolated monomers and their intermolecular interactions with water.

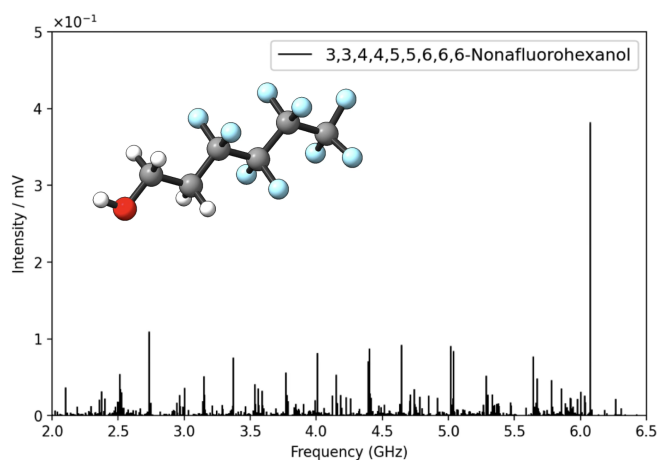


Figure 50: Rotational spectrum of 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexanol (NFH) in the 2.0–6.5 GHz range.

INFRARED AND MICROWAVE SPECTROSCOPY OF (CO)₂ - WATER TRIMERS AND OBSERVATION OF A NEW SYMMETRIC ISOMER

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Weakly bound (CO)₂-water trimers were investigated using high-level *ab initio* calculations together with high-resolution microwave and infrared spectroscopy. Calculations yield a symmetric global minimum structure, Isomer 1, in which two CO molecules form equivalent hydrogen bonds on opposite sides of the water molecule, and a cyclic Isomer 2 containing a single hydrogen bond. Chirped-pulse Fourier-transform microwave measurements provided the first rotational characterization of (CO)₂-D₂O Isomer 2 and significantly extended the known spectrum of (CO)₂-HDO. Small splittings associated with interchange tunnelling of the two CO molecules were determined for both isotopologues. Infrared spectra are observed here for both isomers of (CO)₂-D₂O in the D₂O ν_3 fundamental region near 2780 cm⁻¹, for (CO)₂-HDO Isomer 1 in the O-D stretch region near 2710 cm⁻¹, and for (CO)₂-H₂O Isomer 2 in the ν_2 bend region near 1600 cm⁻¹. The spectrum of Isomer 1 represents the first spectroscopic identification of this structure, with nuclear-spin statistical intensity alternation supporting its C_{2v} symmetry. A large change in the A rotational constant upon vibrational excitation indicates a significant distortion of the geometry. Additional infrared bands were assigned to (CO)₂-H₂O Isomer 2 and tentatively to (CO)₂-HDO Isomer 1.

BRIDGING THEORY AND EXPERIMENT: CO-N₂ 3–0 BAND CASE STUDY

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Carbon monoxide is an important atmospheric trace gas and a sensitive spectroscopic marker in remote sensing of terrestrial and planetary atmospheres [1]. Accurate interpretation of CO absorption spectra requires reliable collisional line-shape parameters, in particular pressure broadening, pressure shift, and velocity-changing collision effects induced by the dominant atmospheric perturbers [2]. Although experimental broadening and shifting data exist for N₂-perturbed CO lines in the second overtone [3,4], comprehensive *ab initio* line-shape parameters, including velocity-changing effects, remain scarce. We present a combined theoretical and experimental study of N₂-perturbed CO transitions in the 3-0 band. The theoretical part is based on fully quantum scattering calculations performed on a recently developed five-dimensional *ab initio* potential energy surface for the CO–N₂ system. The S-matrices obtained by solving the close-coupling (CC) equations were used to calculate generalized spectroscopic cross sections, from which pressure broadening, pressure shift, and Dicke-narrowing parameters were derived [5]. The calculations were carried out with the BIGOS package [6,7] and required extensive convergence analysis with respect to collision energies, number of CC channels, propagation distance, and total angular momenta. Closely spaced ro-vibrational levels of CO, which lead to a large number of CC channels make these calculations particularly demanding.

To validate the theoretical predictions, we performed high-resolution cavity ring-down spectroscopy [8] measurements of CO–N₂ spectra at three temperatures and four pressures. The spectra were recorded with high signal-to-noise ratios, allowing for a stringent test of the calculated line-shape parameters over a broad range of thermodynamic conditions. The comparison between experiment and theory shows very good agreement, demonstrating that fully *ab initio* quantum scattering calculations can reliably describe collisional effects in this diatom-diatom system. The results represent an important step toward populating spectroscopic databases with *ab initio* line-shape parameters of subpercent accuracy.

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NEW BEYOND-VOIGT LINE-SHAPE PROFILE RECOMMENDED FOR THE HITRAN DATABASE

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Advances in high-resolution molecular spectroscopy have shown that the conventional Voigt profile is insufficient for state-of-the-art applications, motivating the development of beyond-Voigt models for spectroscopic databases and atmospheric retrievals. By incorporating speed-dependent collisional broadening and shifting together with Dicke narrowing caused by velocity-changing collisions [1,2], combining them with efficient numerical implementation [3], the Hartmann-Tran (HT) profile [4] became the recommended high-accuracy line-shape model in HITRAN [5]. However, practical applications revealed important limitations, including singular behaviour in the temperature dependence of velocity-changing collision parameters and difficulties in treating gas mixtures. We present a modified Hartmann-Tran (mHT) profile that preserves the physical completeness and computational efficiency of the HT profile while removing its main practical limitations.

The mHT profile [6] is intended as a next-generation beyond-Voigt model for precision spectroscopy and atmospheric applications. It additionally incorporates the β -correction term [7], derived from the more physically justified billiard-ball model [8], improving the treatment of velocity-changing collision and the overall physical consistency of the profile. The model retains computational performance comparable to the HT profile, enabling direct use in large-scale radiative-transfer and spectral-fitting calculations, while naturally supporting line mixing and improved temperature parametrization. The mHT profile is proposed as a new standard for advanced spectral line-shape modelling.

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A COMPLETE ROVIBRATIONAL LEVEL SCHEME FOR NH₃ NEAR 7000 CM⁻¹

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A Complete Rovibrational Level Scheme for NH₃ near 7000 cm⁻¹

The present contribution provides an overview of our recent progress in improving the experimental line list for the ammonia molecule in the infrared range. The target is the 1110 and 0112 band region (6000–8000 cm⁻¹). This analysis extends the recent HITRAN2024 update [1], in which the ammonia spectra were reanalyzed up to 6350 cm⁻¹.

Our goal is a complete (gap-free) list of ammonia rovibrational levels active in this range. To that end, we have analyzed both existing data (sources used for the HITRAN2024 update) and newly recorded spectra in supersonic jet expansion. Finally, the results are compared with the most recent MARVEL analysis [2] as well as the recent evaluation of the HITRAN ammonia spectra by Cacciani and Campargue [3].

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- [1] I.E. Gordon et al., J. Quant. Spectrosc. Radiat. Transf. 353, 109807 (2026).
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- [3] P. Cacciani, A. Campargue, J. Quant. Spectrosc. Radiat. Transf. 109639 (2025).

PRECISION COHERENT MICROWAVE SPECTROSCOPY OF THE R(0) TRANSITION OF OCS IN A KU-BAND WAVEGUIDE

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We report a study of the R(0) transition of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ near 12.16 GHz using a Fourier-transform microwave (FTMW) spectrometer coupled to a 2.6 m Ku-band waveguide cell at room temperature. Line parameters are obtained by non-linear least-squares fitting of the free induction decay in the time domain, over 5 mPa–0.8 Pa, spanning the wall-, Voigt- and collision-dominated relaxation regimes. A quadratic speed-dependent Voigt envelope including wall collisions reproduces the FID down to the noise floor in all three regimes and outperforms Lorentz, Voigt and Galatry models. We report a self-broadening coefficient, a self-shift coefficient of -60(6) Hz/Pa and a population relaxation coefficient of 42(3) kHz/Pa whose zero-pressure intercept, 37(7) kHz, matches the transverse wall-transit rate v_0/b . The line center is reproducible to 12 Hz across three campaigns separated by months, and its overlapping Allan deviation averages as $\tau^{-1/2}$ to 2×10^{-11} near $\tau = 2000$ s. Accuracy, however, is limited by an effect we did not anticipate: the fitted line center depends on the pulse area of the excitation, drifting by several hundred Hz between the zero-field extrapolation and the nominal $\pi/2$ condition, and excursions by several kHz near integer multiples of π where the FID phase flips. Because the signal is detected background-free, this should not be an AC Stark shift. We discuss candidate mechanisms for this pulse-area dependence.

ACCURATE ROVIBRONIC LINE LISTS OF HYDROGEN FLUORIDE

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²Beirut Arab University, Department of Physics, Beirut, 11-5020, Lebanon

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Hydrogen fluoride (HF) is the dominant fluorine-bearing molecule in the interstellar medium and an important tracer of molecular hydrogen (H₂) in star-forming regions.¹ Its astronomical detection has been confirmed by the *Infrared Space Observatory* (ISO) and the *Herschel Space Observatory*.² Accurate spectroscopic data for HF are essential for interpreting astronomical observations and for atmospheric retrievals from current and future space missions, including the *James Webb Space Telescope* (JWST) and ESA's *Ariel* mission.³ Despite its astrophysical importance, comprehensive and highly accurate rovibronic line lists covering the low-lying excited electronic states remain limited.

In this work, we construct an accurate spectroscopic model for the $X^1\Sigma^+$, $B^1\Sigma^+$, and $C^1\Pi$ electronic states of HF by combining experimentally derived energy levels with high-level *ab initio* calculations. Line positions are improved by using both laboratory and astronomical observational spectra through the MARVEL (Measured Active Rotational–Vibrational Energy Levels) procedure⁴, while transition dipole moment curves are employed to calculate transition intensities. The refined model is used to generate rovibronic energy levels, transition frequencies, Einstein *A* coefficients, and comprehensive line lists in the ExoMol format. The resulting line lists provide accurate rovibronic data suitable for astrophysical applications, including molecular identification in astronomical spectra and atmospheric modeling of exoplanets and cool stars.

¹ D. A. Neufeld and M. G. Wolfire, *Astrophys. J.* **706**, 1594–1607 (2009).

² D. A. Neufeld, M. Agúndez, M. Gerin, *et al.*, *Astron. Astrophys.* **518**, L108 (2010).

³ K. L. Chubb, S. Robert, C. Sousa-Silva, S. N. Yurchenko, *et al.*, *RAS Tech. Instrum.* **3**, 636–690 (2024).

⁴ T. Furtenbacher, A. G. Császár, and J. Tennyson, *J. Mol. Spectrosc.* **245**, 115–125 (2007).

WIDE-RANGE FROST-POINT MEASUREMENT USING A CRDS-BASED MINIATURIZED SENSOR

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In the development and manufacturing of high-tech products such as Li-ion batteries and organic light-emitting diodes (OLEDs), low frost-point environments with frost points ranging from -30°C to -70°C are required. To control the frost point of dry gases in such environments, various frost-point hygrometers are employed, including capacitive sensors and chilled-mirror hygrometers. However, these methods rely on the capture of water vapor at the sensor surface and require a waiting time for equilibrium to be established. As a result, their response time is limited, particularly in the low frost-point region.

Cavity ring-down spectroscopy (CRDS) has become a standard technique for measuring trace moisture in gases below $1\text{ }\mu\text{mol/mol}$ (1 ppm) in amount fraction (corresponding to a frost point of -75°C at atmospheric pressure). This method offers several advantages, including high sensitivity, immunity to interference from ambient moisture outside the cavity, and an inherently absolute measurement principle. These features suggest that CRDS could also be effective for humidity measurements at higher concentration ranges. Nevertheless, its application to frost-point measurements above -70°C has rarely been reported.

In this study, we developed a CRDS-based frost-point hygrometer for measurements in the range of -10°C to -70°C . The measurement system is based on a previously developed miniaturized CRDS sensor (mini-CRDS) for trace-moisture measurement. The performance was evaluated by comparison with a primary low frost-point standard previously developed at the National Metrology Institute of Japan (NMIJ).

Challenges associated with extending CRDS to frost-point measurements at higher frost-point ranges will be discussed.

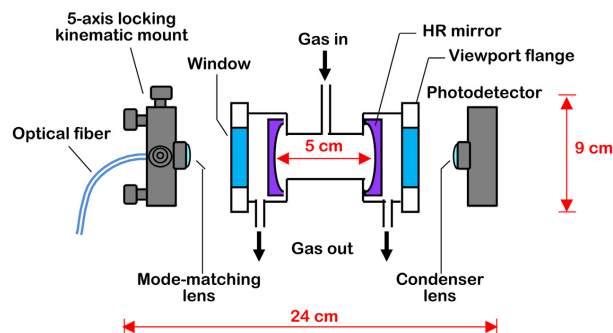


Figure 51: Schematic diagram of a mini-CRDS sensor

EXPLORING HIGH AND LOW METHYL TORSIONAL BARRIERS IN 2-CHLOROPICOLINES: THE MICROWAVE SPECTRA OF 2-CHLORO-3-PICOLINE AND 2-CHLORO-PICOLINE

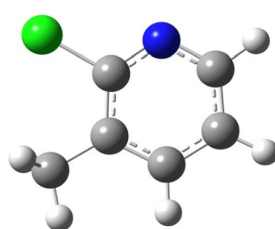
M. Buttkus-Barth¹, H. V. L. Nguyen^{1,2}

¹Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France

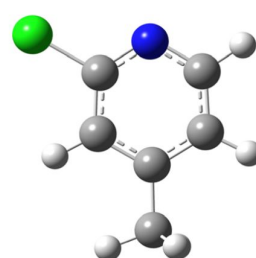
²Institut Universitaire de France (IUF), F-75231 Paris, France

Last year, we presented at HRMS the rotational spectroscopic analysis of 2-chloro-5-picoline, the first molecule to the best of our knowledge containing a methyl internal rotation with both chlorine and nitrogen nuclear quadrupole coupling interactions.¹ Building on this work, we have investigated two additional members of the 2-chloropicoline series: 2-chloro-3-picoline and 2-chloro-4-picoline. These two molecules represent opposite regimes of methyl internal rotation: 2-chloro-4-picoline exhibits a low torsional barrier, whereas 2-chloro-3-picoline possesses a comparatively high barrier. Therefore, the interaction between the A-E torsional fine splittings and the combined chlorine and nitrogen hyperfine structure presents different spectroscopic challenges for the two molecules.

In this poster, we report the successful assignment of the microwave spectra of both molecules using broadband survey spectra recorded between 6.0 and 20.0 GHz with the chirp-excitation mode of the PARIS (Passage And Resonance In Synergy) spectrometer, complemented by some additional measurements obtained in the resonator mode.² The spectra were analyzed using the *XIAM_2NQ* program,³ a modified version of *XIAM*⁴ that treats exactly the nuclear quadrupole coupling of up to two atoms with quadrupolar moments, yielding fits for both molecules with root-mean-square deviations close to the measurement accuracy of 2 kHz for both modes of the PARIS spectrometer. The experimentally determined torsional barriers of 497.8 cm⁻¹ for 2-chloro-3-picoline and 36.9 cm⁻¹ for 2-chloro-4-picoline, as well as the nuclear quadrupole coupling constants, are compared with those of other picolines.⁵



2-chloro-3-picoline



2-chloro-4-picoline

¹M. Buttkus-Barth, S. Herbers, H. V. L. Nguyen, *A chlorine, a nitrogen, and a methyl rotor: 2-chloro-5-picoline analyzed by microwave spectroscopy and quantum chemical calculations* [Presentation], 29th Colloquium on High-Resolution Molecular Spectroscopy, Cologne (2025).

²H. V. L. Nguyen, S. Herbers, X. Landsheere, J.-U. Grabow, *Rev. Sci. Instrum.* **96**, 054706 (2025).

³S. Herbers, W. Li, P. Buschmann, M. Li, J.-U. Grabow, A. Lesarri, *J. Chem. Phys.* **162**, 234304 (2025).

⁴H. Hartwig, H. Dreizler, *Z. Naturforsch.* **51a**, 923 (1996).

⁵M. Buttkus-Barth, *Coupled large amplitude motions in picoline derivatives investigated by microwave spectroscopy and quantum chemistry*, PhD thesis, Université Paris-Est Créteil, France (2025).

TORSIONAL VIBRATIONS AND SYMMETRY OF B(OH)₃: TESTING THE UNITED CONFIGURATION APPROACH TO SELECTED NON-RIGID MOLECULES

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The boric acid (BA) molecule has long been known and is widely used in everyday life and chemical production. A number of studies have confirmed the existence of this molecule in the gas phase. As well-known BA is a non-rigid molecule. As a rigid object it can exist in two conformations having C_{3H} and C_S point symmetry groups (PSG). Both are flat. C_{3H} conformer can exist in two equivalent versions and C_S conformer — in six equivalent versions. As C_{3H} has order 6 and C_S — order 2 the molecular symmetry group (MSG) has to have order 12. The MSG of BA can readily be identified as D_{3H}(M). Using “united” BA configuration, which allows to obtain any version of the both conformers by deleting three hydrogen atoms, it is possible to set internal coordinate system and to find isomorphic PGS (IPGS). According D_{3H}(M) full wave function (WF) have to belong to A₁'' or A₂''. Eight combinations of the nuclear spin WF are represented as 4 A₁' + 2 E'. In the D_{3H}(M) each A'' vibration of the C_S conformer splits due to tunneling into the following pair A'' ⇒ A₁'' + A₂'' as well as each A'' vibration of the C_{3H} conformer. However, each E'' torsional vibration does not really split but simply doubles. The following combinations of torsional and spin wave functions species are permissible: A₁'' and A₂'' with A₁', and E'' with E', respectively.

3D PES of the BA molecule was calculated using MP2/CBS(aug-pVDZ,aug-pVTZ,aug-pVQZ) level of theory. Kinetic energy operator for torsional coordinates was determined in frame of Wilson $\vec{s}$ formalism. All symmetry properties were taken into account¹. Vibrational Schrödinger equation of restricted dimensionality was solved by using complex Fourier series^{2,3,4}. According to results of calculations the ZPVE is 758.8 cm⁻¹. Tunneling splitting of the ground state is 3×10⁻¹² cm⁻¹. Frequency of A'' and E'' torsional vibrations in the C_{3H} conformer are 459.5 and 520.9 cm⁻¹, while splittings of these vibrational states are 8.1×10⁻⁹ and 1.0×10⁻¹⁸ cm⁻¹ (the latter value is at the limit of computational accuracy). The energy of the C_S conformer is on 1384.9 cm⁻¹ higher than C_{3H} one. Splittings of the 6 ground torsional states of the C_S conformer are more complicated: ΔE_{i+1,i} = E_{i+1} - E_i: 1.8×10⁻² (i=1), 7.3×10⁻¹² (i=2), 2.6×10⁻¹ (i=3), 6.3×10⁻¹² (i=4), 1.8×10⁻² (i=5) (all data in cm⁻¹).

¹G. Pitsevich, A. Malevich, A. Kamnev, Spectrochim.Acta Part A, **327** (2025) 125307.

²G. Pitsevich, A. Malevich, Opt.Phot.J., **2** (2012) 332–337.

³G. Pitsevich, A. Malevich, J.Mol.Spectr., **404** (2024) 111937.

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CAN DVR AND FOURIER METHODS REPRODUCE THE EXACT $(2\ell + 1)$ — FOLD DEGENERACY OF THE FREE RIGID ROTOR?

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As is well known, there are not too much problems in quantum mechanics that have an exact analytical solution. One of such problems is finding the energies of the stationary states of a free rigid rotor. This can be a particle of mass m rotating around a point at a constant distance. The Schrödinger equation for such a quantum mechanical system has the following form:

Levels number (n)	DVR method		Fourier method		Analytical solution	
	E_n	$E_n - E_{n-1}$	E_n	$E_n - E_{n-1}$	E_n	$E_n - E_{n-1}$
1	0	—	0	—	0	—
2	30	30	30	30	30	30
3	30	2.3×10^{-11}	30	3.7×10^{-31}	30	0
4	30	2.3×10^{-11}	30	3.7×10^{-31}	30	0
5	90	60	90	60	90	60
6	90	4.1×10^{-11}	90	3.9×10^{-31}	90	0
7	90	4.1×10^{-11}	90	3.9×10^{-31}	90	0
8	90	4.1×10^{-11}	90	3.9×10^{-31}	90	0
9	90	4.1×10^{-11}	90	3.9×10^{-31}	90	0

$$-\frac{\hbar^2}{2ma^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \Psi = E\Psi. \quad (1)$$

In equation (1), the angular coordinate θ varies in the interval from 0 to π , and the angular coordinate φ varies in the interval from 0 to 2π . Let us rewrite equation (1) in the following:

$$-F \operatorname{ctg} \theta \frac{\partial \Psi}{\partial \theta} - F \frac{\partial^2 \Psi}{\partial \theta^2} - F \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \varphi^2} = E\Psi; \quad F = \frac{\hbar^2}{2ma^2}. \quad (2)$$

The energy of a free rigid rotor is defined by the relation $F_l = Fl(l+1)$, where l takes non-negative integer values starting from zero. Furthermore, the energy of a rigid rotor is $2l+1$ times degenerate in the quantum number m_l . Clearly, if we set the constant F equal to 15 cm^{-1} , then the energies of the first nine stationary levels of the rotor must be exactly equal to 0, 30, 30, 30, 90, 90, 90, 90, 90 cm^{-1} . The energies of the free rigid rotor were calculated using DVR^{1,2} and Fourier³ methods on the same grid. The results are presented in Table.

An analysis of the data in Table shows that both methods demonstrate excellent results when the values of the kinetic parameters at various points of the angular coordinates can be calculated accurately. However, it is obvious that the Fourier method reproduces the degeneracy of the energy levels more accurately (at the limit of the specified program accuracy of the Mathematica package) compared to the DVR method. This means that when solving problems with a known hyperfine splitting of energy levels involving angular and especially periodic angular vibrational coordinates, the Fourier method is preferable to the DVR method⁴.

¹D.O. Harris, G.G. Enderholm, W.D. Gwinn, J. Chem. Phys. **43** (1965) 1515-1517.

²J.C. Light, I.P. Hamiltonian, J.V. Lill, J. Chem. Phys. **82** (1985) 1400.

³G. Pitsevich, A. Malevich, Opt.Phot.J., **2** (2012) 332-337.

⁴G. Pitsevich, A. Malevich, A. Kamnev, Spectrochim. Acta Part A, **327** (2025) 125307.

I: Invited Speakers

Wednesday, September 02, 2026, 09:00

Chair : Konstantin Vodopyanov

OPTICAL FREQUENCY COMB SPECTROSCOPY IN COLD AND NON-EQUILIBRIUM MOLECULAR ENVIRONMENTS

Lucile Rutkowski¹

¹Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France

Optical frequency comb Fourier transform spectroscopy has become a powerful tool for broadband, high-resolution molecular spectroscopy. Here, recent developments extending this approach to low-temperature and non-equilibrium environments relevant to laboratory astrophysics and molecular reaction dynamics will be presented.

The key advance is the implementation of sub-nominal-resolution comb-based Fourier transform spectroscopy in cold and reactive media. Broadband cavity-enhanced spectroscopy in supersonic jet expansions, providing frequency-calibrated spectra of isolated cold molecules with accurate determination of rovibrational line parameters will be demonstrated. The combination of cavity enhancement, intrinsic comb frequency calibration and self-referenced acquisition enables robust measurements while preserving both high spectral resolution and broad bandwidth.

The technique has also been extended to pulsed plasma sources, where transient species and strongly non-equilibrium rovibrational populations can be investigated. Time-resolved frequency comb Fourier transform spectroscopy provides simultaneous spectral and temporal resolution, allowing the evolution of reactive molecular systems to be monitored on experimentally relevant timescales.

These developments establish frequency comb Fourier transform spectroscopy as a versatile platform for quantitative spectroscopy in environments that have traditionally been difficult to access with broadband high-resolution techniques. Applications to laboratory astrophysics and state-resolved studies of low-temperature reaction dynamics will be discussed.

PRECISION COLLISIONAL LINE-SHAPE ANALYSIS AND QUANTUM GAS METROLOGY VIA ALL-FREQUENCY-DOMAIN SPECTROSCOPY

Yan Tan^{1,2}, Shui-Ming Hu^{1,2}, Jin Wang^{1,2}, Jin-Ke Li^{1,2}, Qi Huang^{1,2}, Hui Liang^{1,2}, Chang-Le Hu^{1,2}

¹Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

²Hefei National Laboratory, Hefei 230088, China

As measurement sensitivity approaches the parts-per-million (ppm) level, the fidelity of scientific conclusions is no longer limited by instrument sensitivity, but depends on the ability to accurately distinguish genuine physical effects from subtle systematic artifacts embedded in the data analysis process, spectral line shape models, and experimental baselines. Here we propose a unified framework—by fully utilizing all frequency-domain information encoded in cavity-enhanced dispersive spectroscopy, we advance the study of the physics of collision spectral line shapes while establishing a new paradigm for quantum gas metrology that is directly traceable to the International System of Units (SI).

Collisional line-shape analysis. We developed a hierarchical self-consistency framework: high- J ratios act as pressure-independent null controls, low- J symmetric ratios test integral-area extraction under strong broadening, and cross- J ratios ($R1/R10$) probe the claimed J -dependence. AIC/BIC model selection makes line-shape choice objective; only the Hartmann–Tran profile is retained over the full pressure range. We find **no statistically significant pressure dependence** in $R1/R10$.

Quantum gas metrology. DW-CMDS intensity ratios achieve fractional uncertainties of 3×10^{-5} (30~ppm) — a 30-fold advance over the prior 0.1% benchmark — enabling line-ratio thermometry (LRT) competitive with established primary methods: the CO $R(0)/R(20)$ pair yields 0.5~mK statistical and 2.0~mK systematic uncertainty at 298~K. Extending to H_2 (2–0) quadrupole transitions, we determine an $S(0)/Q(1)$ transition-rate ratio of $0.657448(16)_{\text{stat}}(85)_{\text{sys}}$ with an Allan deviation of 4×10^{-5} (~ 12 ~mK). The ratio agrees with non-adiabatic perturbation theory at $-0.11(15)$ ‰, while absolute intensities deviate by up to $-1.48(37)$ ‰, exposing missing relativistic (α^2) and finite-nuclear-mass corrections in the current H_2 quadrupole-moment theory. These results establish DW-CMDS as a molecule-agnostic platform for fundamental molecular physics and primary thermometry, with a clear path toward 10^{-6} -level measurements.

**J: Mini Symposium: Molecular Ion
Spectroscopy**

Wednesday, September 02, 2026, 11:00

Chair : José Luis Doménech

REVEALING HIGH-RESOLUTION SPECTRA OF HYDROCARBON CATIONS WITH LEAK-OUT SPECTROSCOPY

Oskar Asvany¹, Philipp Schmid¹, Wesley Silva¹, Divta Gupta¹, Samuel J. P. Marlton¹, Thomas Salomon¹, and Stephan Schlemmer¹

¹I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

Molecular ions, in particular hydrocarbon cations, are key intermediates driving the chemistry of the interstellar medium through ion–molecule reactions. Although some of these species have been known for decades in the interstellar medium - CH^+ being the first molecular ion ever detected¹ - in recent years, some more of these ions have been observed, the most spectacular one being the discovery of CH_3^+ with the James Webb Space Telescope (JWST) toward the UV-irradiated protoplanetary disk d203-506 in the Orion bar². However, high-resolution laboratory data for many other hydrocarbon cations are still lacking, making them elusive to both astronomers and experimentalists. With the advent of leak-out spectroscopy (LOS³), high-resolution rovibrational spectra of many bare ions, long missing, can now be recorded with unprecedented signal-to-noise ratio. In addition, by applying a rotational-rovibrational double resonance version of LOS⁴, also pure rotational spectra can be recorded for these species, laying the basis for their potential detection in space. This talk reviews the detection history of these species and presents recent laboratory results for some astrophysically relevant hydrocarbon cations, including CH_3^+ , as well as isomers of C_3H_3^+ and C_3H_2^+ .

¹Douglas and Herzberg, *Astrophys. J.* 94, 381 (1941)

²Berné et al, *Nature* 621, 56 (2023)

³Schmid et al., *J. Phys. Chem. A* 126, 8111 (2022)

⁴Asvany et al., *PCCP* 25, 19740 (2023)

DEUTERONATED FORMALDEHYDE IN FOCUS: THEORY AND EXPERIMENT

Denis Comte¹, Mattia Melosso², Hunarpreet Kaur^{3,4}, Dennis F. Dinu², Ernest A. Michael⁵, Terri E. Field-Theodore¹, Wesley G. D. P. Silva⁵, Silvia Alessandrini², Luca Bizzocchi², Sven Thorwirth⁵, Klaus R. Liedl⁶, Sandra Brünken^{3,4}, Cristina Puzzarini², Stephan Schlemmer⁵, Oskar Asvany⁵

¹Scuola Superiore Meridionale, Naples, Italy

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³HFML-FELIX, Nijmegen, The Netherlands

⁴Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

⁵I. Physikalisches Institut, Universität zu Köln, Germany

⁶Department of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Austria

Deuteronated molecular ions are important intermediates in the gas-phase chemistry of cold interstellar environments, where they can drive molecular deuteration. However, only a small number of such ions, including DCO⁺ (Hollis *et al.*, *Astrophys. J.*, 1976), N₂D⁺ (Snyder *et al.*, *Astrophys. J.*, 1977), DCS⁺ (Fuentes *et al.*, *Astron. Astrophys.*, 2016), and NH₃D⁺ (Cernicharo *et al.*, *Astrophys. J. Lett.*, 2013), have been detected in space, mainly because accurate laboratory spectra are often missing for more complex species.

Here, we present the first experimental spectroscopic characterization of deuteronated formaldehyde, H₂COD⁺, which is predicted to be the most abundant deuterated isotopologue of protonated formaldehyde in prestellar cores (Osamura *et al.*, *Astrophys. J.*, 2005). Broadband infrared spectra were recorded using Ne-tagging infrared predissociation (IRPD) and leak-out spectroscopy (LOS) and assigned with the support of high-level anharmonic calculations (Comte *et al.*, *Chem. Phys. Lett.*, 2026). These data then guided high-resolution measurements of the hybrid *a*- and *b*-type ν_1 rovibrational band, shown in Figure 1, and of 36 pure rotational transitions (Comte *et al.*, manuscript under revision for *Phys. Chem. Chem. Phys.*). The resulting spectroscopic constants enable future radioastronomical searches for H₂COD⁺. Altogether, this work provides a showcase of state-of-the-art molecular-ion spectroscopy, combining high-level coupled-cluster composite methods and vibrational configuration interaction (VCI) calculations with broadband and high-resolution rovibrational and rotational LOS.

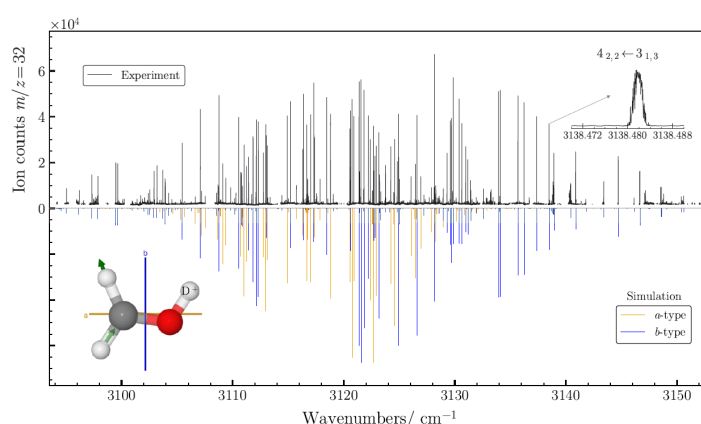


Figure 52: Comparison between the experimental (top) and simulated (bottom) spectra of the ν_1 band of H₂COD⁺. Insets show (upper right) a single rovibrational transition and (lower left) the molecular structure with the ν_1 vibrational motion indicated by green arrows.

HIGH RESOLUTION ROVIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF HC_3N^+

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Cyanopolyynes (HC_{2n+1}N where $n = 1, 2, 3, \dots$) are key constituents of interstellar chemistry and have been observed across a wide range of astrophysical environments, including from cold molecular clouds to external galaxies. The simplest member of this family, cyanoacetylene (HC_3N), was among the first organic molecules discovered in space by radio astronomy being identified toward Sgr B2 as early as 1971.¹ More recently, the corresponding radical cations of several cyanopolyynes, i.e. HC_3N^+ , HC_5N^+ , and HC_7N^+ have also been detected in interstellar medium.² As no high-resolution laboratory data are available to support their astronomical identification, these detections were solely done based on quantum chemical calculations. Here, we present the first spectroscopic data for HC_3N^+ obtained using the leak-out spectroscopy (LOS) technique in a 22-pole cryogenic ion trap apparatus.³ Rovibrational transitions within the C–N stretching mode (ν_2) at around 2170 cm^{-1} were first measured at 40 K. As HC_3N^+ is a linear open-shell species with one unpaired electron, the observed transitions show resolved characteristic splittings arising from both spin–orbit and Λ -doubling fine structure components. Based on a preliminary fit of the rovibrational data, we searched for ground state rotational transitions of HC_3N^+ using a IR/mm-wave double-resonance scheme based on LOS. Over ten transitions were observed between 80 and 250 GHz. Together, the high-resolution laboratory data reported here enable a significant improvement of the spectroscopic constants and confirm the astronomical detection of this important cation.

¹Turner, *Astrophys. J.*, 163, L35, 1971

²Cabezas *et al.*, *A&A*, 687, L22, 2024

³Schmid *et al.*, *J. Phys. Chem. A*, 126, 43, 8111–8117, 2022

HIGH-RESOLUTION SPECTROSCOPY OF ELUSIVE PROTONATED METHANOL (CH_3OH_2^+)

Wesley G. D. P. Silva¹, Oskar Asvany¹, Sven Thorwirth¹, Isabelle Kleiner², Iwona Gulaczyk³, Marek Kreglewski³, Miguel Sanz-Novo⁴, Victor M. Rivilla⁵, and Stephan Schlemmer¹

¹I. Physikalisches Institut, Universität zu Köln, Germany

²Université Paris Cité and Université Paris-Est Créteil, CNRS, LISA, France

³Faculty of Chemistry, Adam Mickiewicz University, Poland

⁴Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Germany

⁵Centro de Astrobiología (CAB), INTA-CSIC, Spain

Although considered one of the most important species driving chemical complexity in space, protonated methanol (CH_3OH_2^+) remains elusive to astronomers due to the lack of laboratory spectroscopic data required to guide its astronomical detection. In this work, we report the first high-resolution spectra of CH_3OH_2^+ , measured in a cryogenic ion trap instrument using leak-out spectroscopy (LOS) [1]. Rovibrational transitions within the fundamental C–H and O–H stretching modes were initially recorded near 3000 cm^{-1} and 3500 cm^{-1} , respectively. Because CH_3OH_2^+ exhibits two large-amplitude motions, internal rotation of the CH_3 group and inversion of the OH_2 group, the observed spectra contain multiple tunneling components, making them extremely challenging to assign.

Despite this complexity, several series of transitions were successfully assigned with the aid of quantum chemical calculations, providing the first set of ground-state spectroscopic parameters for CH_3OH_2^+ . These rovibrational data were subsequently used to search for pure rotational transitions of CH_3OH_2^+ in the 40–350 GHz frequency range using an infrared/millimeter-wave double-resonance scheme [2]. This combined experimental approach has so far enabled the measurement of more than 25 rotational transitions of CH_3OH_2^+ . Based on the accurate transition frequencies derived in this work, the first astronomical searches for this important cation are now in progress.

[1] J. Phys. Chem. A, 126, 8111, 2022

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ELECTRONIC LEAK-OUT SPECTROSCOPY OF COLD ASTROPHYSICALLY RELEVANT IONS IN THE GAS PHASE AND SEARCH FOR DIBS.

Le Schneider¹, Samuel J. P. Marlton¹, Eline Plaar¹, Robin Jacobi¹

¹University of Cologne, Department of Physics

Diffuse interstellar bands (DIBs) are absorption features in the spectra of stars. They are widely accepted to originate from molecules, and were first discovered by Mary Lea Heger.¹ There are over 500 DIBs, which appear in the nIR, visible and UV light range. Thusfar only 5 DIBs were assigned to one carrier, C₆₀⁺.² An ideal method to study DIBs would be a method that can give us high resolution spectra of bare ions that do not dissociate in the visible light. Leak out spectroscopy (LOS) enables us to measure spectra of bare ions in the gas phase in a one photon process. Photoexcited ions collides with buffer gas in a cryogenically cooled ion trap, which leads to an energy transfer from internal energy into translational energy, allowing the ion to leave the trap. This ion count is plotted as a function of the laser frequency, which yields the spectrum.³ Electronic leak out spectroscopy (eLOS) has been done in the visible using a low resolution continuous light source.⁴ In order to look for DIBs, we implemented eLOS for the first time with a high resolution pulsed laser. To validate this new setup, we began with the well known diacetylene cation. We measured A ²Π_u – X ²Π_g vibronic transitions. This method appears to be sensitive, as we see A ²Π_{1/2} – X ²Π_{3/2} spin forbidden transitions for the first time and are able to resolve rotational structures (see Figure 1).

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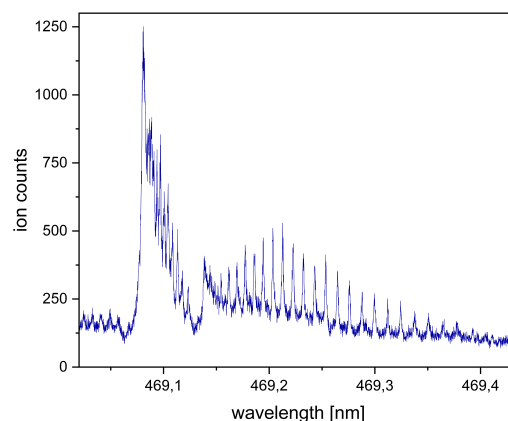


Figure 53: Spectrum of A ²Π_{3/2} – X ²Π_{3/2} transition of Diacetylene cation in the gas phase measured with leak out spectroscopy (LOS).

K: Ioannes Marcus Marci Session

Wednesday, September 02, 2026, 16:30

Chair : José Cernicharo

MASSIVE BLACK HOLES AND GALAXIES: EXPERIMENTAL EVIDENCE AND COSMIC CO-EVOLUTION

Reinhard Genzel¹

¹Max-Planck-Institut for Extraterrestrial Physics, Garching, Germany

More than a century ago, Albert Einstein presented his general theory of gravitation. One of the predictions of this theory is that not only particles and objects with mass, but also the quanta of light, photons, are tied to the curvature of space-time, and thus to gravity. There must be a critical mass density, above which photons cannot escape. These are black holes.

Most galaxies host massive black holes of masses between millions to billions of solar masses at their nuclei, which can become active galactic nuclei and quasars when they accrete gas and stars rapidly. I will discuss the major progress that has happened in the last decades to prove the massive black hole paradigm through ever more detailed, high-resolution observations, in the center of our own Galaxy, as well as in external galaxies. In the Galactic Center such high-resolution observations can also be used to test General Relativity in the regime of large masses and curvatures. I will also discuss very recent observations that there are massive black holes already a few hundred Myrs after the Big Bang.

L: Invited Speakers

Thursday, September 03, 2026, 09:00

Chair : Cristóbal Pérez

PUTTING LIGHT TO CHEMICAL USE: FROM SPECTATOR TO ACTIVATOR

Wybren Jan Buma^{1,2}

¹Van 't Hoff Institute for Molecular Sciences, Faculty of Science, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

²Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands

The interaction between light and matter is at the basis of research aimed to elucidate chemical, physical and biological processes at the molecular level. As such, it enables one to probe molecular structure and reactivity in a wide range of application hard to analyse by conventional methods. In the present contribution I will illustrate this with two recent examples in which we use infrared absorption spectroscopy under molecular beam conditions to provide fingerprints of structure and reactivity.

In the first I focus on the origin of Aromatic Infrared Bands (AIBs), emission features observed ubiquitously across a wide variety of interstellar objects. As yet, they have tacitly been assumed to arise from radiative cooling of vibrationally hot electronic ground states. For neutral PAHs it is well known, however, that intersystem crossing to the triplet manifold is a competing -and often dominating- relaxation channel. What so far has been notoriously missing to determine the contribution of such PAH triplet states are laboratory studies of their infrared absorption spectra under astronomically relevant conditions. I will present a novel experimental approach that has enabled us to record for the first time such spectra and discuss their implications for astronomical models.

In the second I will present recent work on elucidating catalytic reaction mechanisms and in particular to shed light on the reactive intermediates involved in catalytic reactions. For reactions involving charged species impressive progress has been made using mass-spectrometry based methods, but for reactions involving neutral species such information has for all practical purposes been impossible to obtain. Using a thiourea catalysed Michael addition reaction I will show how we are able to trap and study reactive and non-reactive assemblies of catalyst and reactants using molecular beams, and in fact ultimately perform homogenous catalysis *in vacuo*.

Light can, however, also be used to activate molecules and materials and to transform photon energy into mechanical, electrical and chemical energy. State-of-the-art gas- and solution-phase spectroscopic techniques in combination with advanced quantum chemical calculations enable nowadays a direct monitoring of the processes occurring on the molecular scale after the photon has been absorbed. As such, they form the basis for optimizing and coming to the rational design of novel photoactive materials. In the present contribution I will discuss our efforts to meet the growing demand for materials capable of efficiently converting light into heat, with applications ranging from sunscreens in healthcare to crop enhancement in agriculture.

CHIRAL MOLECULES ACROSS ROTATIONAL, VIBRATIONAL AND ELECTRONIC SCALES: FROM MOLECULAR FINGERPRINTS TO ENANTIOSELECTIVE DETECTION AND CONTROL

Thomas Giesen¹

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Chiral molecules are of broad relevance in chemistry, biology and astrochemistry. Since conventional spectroscopic measurements do not distinguish between enantiomers, enantiomer-sensitive detection remains a particular challenge. High-resolution gas-phase spectroscopy provides the structural and dynamical information required to identify suitable molecular systems and to develop corresponding experimental approaches. Addressing this challenge requires complementary techniques spanning the microwave to optical regions, together with cold and well-controlled molecular samples.

Enantiomer-sensitive detection by microwave three-wave mixing has been demonstrated using purely rotational transition cycles. Theoretical studies have shown that this concept can be extended by incorporating rovibrational transitions, opening possible routes toward hybrid schemes that combine microwave or millimeter-wave radiation with infrared excitation.

The development of such experiments requires molecular candidates whose structures, transition moments, internal dynamics and spectral complexity are sufficiently well understood. Equally important are techniques for the state-selective preparation and detection of molecules across the relevant spectral regions.

This talk presents selected results and perspectives along this path. Studies of propylene oxide, styrene oxide and related candidate molecules provide insight into molecular structure, large-amplitude motion, state mixing and excitation-dependent dynamics. Infrared excitation combined with millimeter-wave detection gives access to state-selective population changes, collisional redistribution and coherence in supersonic jets. Complementary IR-REMPI experiments demonstrate that high-resolution infrared excitation can be combined with conformer- and state-selective electronic detection.

Together, these studies represent steps toward connecting molecular characterization, state-selective preparation and coherent detection across rotational, vibrational and electronic energy scales. The talk will conclude with perspectives on promising molecular candidates and on the experimental requirements for extending gas-phase enantiomer-sensitive spectroscopy beyond established microwave approaches.

**M: Mini Symposium: Chirality and Chiral
Recognition**

Thursday, September 03, 2026, 11:00

**Chair : Maria Eugenia Sanz and Melanie
Schnell**

TESTING MECHANISMS FOR ASYMMETRIC SYNTHESIS USING CHIRAL TAG ROTATIONAL SPECTROSCOPY

Brooks H. Pate¹

¹Department of Chemistry, University of Virginia

The development of asymmetric synthesis methods presents challenges for chiral analysis. Successful synthetic chemistry approaches must produce chiral reaction products in high enantiopurity. Methods for measuring the enantiomeric excess of newly synthesized molecules are needed to establish the scope of reaction for the synthetic methodology. Ultimately, there is interest in elucidating the mechanism of the synthetic method and this requires assigning the absolute configuration of the reaction product. Analytical chemistry methods for correct assignment of absolute configuration of newly synthesized compounds are relatively limited. Molecular rotational spectroscopy has developed two approaches to chiral analysis in the past decade: microwave three-wave mixing and chiral tag rotational spectroscopy. In chiral tag rotational spectroscopy, enantiomers of the analyte are converted to spectroscopically distinct diastereomers through formation of a noncovalent complex with a small, chiral molecule (the tag). The advantages of this approach for applications in asymmetric synthesis will be described. Recent examples of chiral analysis performed by chiral tag rotational spectroscopy to elucidate the mechanism of new asymmetric synthesis methodologies will be presented.

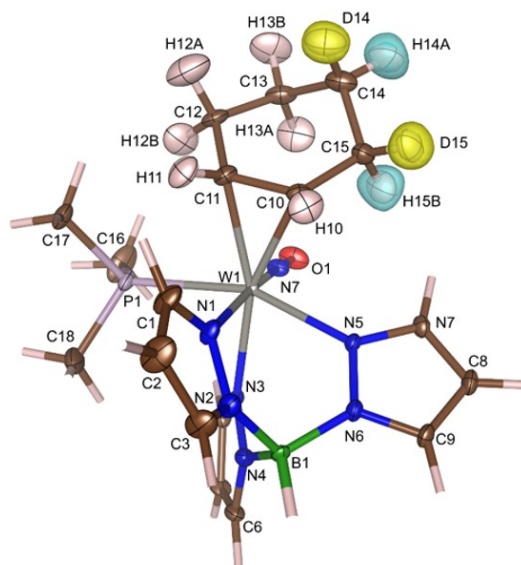


Figure 54: Tungsten Transition Metal Complex for Precision Deuteration Chemistry

VIBRATIONAL SPECTROSCOPY AND PHOTOELECTRON CIRCULAR DICHROISM OF CHIRAL COMPLEXES

Anne Zehnacker¹

¹Institut des Sciences Moléculaires d'Orsay. CNRS and University Paris Saclay. France

Molecular interactions are strongly sensitive to chirality and conformational flexibility. We use laser-spectroscopy methods that allow probing both molecular properties simultaneously. On the one hand, conformer-selective double resonance spectroscopy is a versatile probe of the structure of weakly bound complexes of chiral molecules, such as those involved in molecular recognition in biological environments or chiral-phase chromatography. On the other hand, PhotoElectron Circular Dichroism (PECD), defined as a forward-backward asymmetry in the angular distribution of the photoelectrons emitted by a chiral molecule photoionised by circularly polarised light (CPL), is very sensitive to structure and aggregation. We recently developed a PECD scheme based on a two-photon ionisation process, which allows obtaining the PECD of each conformer of a chiral molecule separately. This experiment was applied to flexible chiral molecules and their weakly bound complexes in the gas phase. We studied in particular the influence of complexation by a chiral tag on the PECD of a chiral chromophore or the appearance of induced chirality in an achiral chromophore due to its complexation with a chiral molecule.

SPIN-CHIRALITY COUPLING WITHOUT MAGNETIC FIELDS

Philip Flores¹, Stefanos Carlström¹, Serguei Patchkovskii¹, Misha Ivanov^{1,2,3}, Andres Ordonez^{1,4,5},
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²Institute of Physics, Humboldt University zu Berlin, 12489 Berlin, Germany

³Technion - Israel Institute of Technology, Haifa, Israel

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Chirality underlies a wide range of phenomena in molecular physics, chemistry, and biology, giving rise to observables that reverse sign between enantiomers. In photoionization, the most prominent example is photoelectron circular dichroism (PECD), where circularly polarized light induces a forward-backward asymmetry in electron emission within the electric dipole approximation [1]. Beyond angular asymmetries, the photoelectrons can also be spin-polarized, opening an additional enantio-sensitive channel driven by spin-orbit coupling, and scattering dynamics. Recent discovery of chirality-induced spin selectivity (CISS) has revealed unexpectedly strong spin filtering in chiral systems [2], raising fundamental questions about the dynamical origins of spin-chirality coupling.

Here, we demonstrate that spin-resolved one-photon ionization of randomly oriented chiral molecules is governed by a universal geometric structure: all spin-polarized and enantio-sensitive observables are controlled by the same three pseudovectors. These pseudovectors generate the molecular pseudoscalars that determine enantio-sensitive signals and define the angular distribution of spin polarization, which we show to be enantio-sensitive even when the total spin-polarization is not [3]. This framework further reveals that the photoelectron spin and momentum are enantio-sensitively ‘locked’, forming spin-current correlations with a clear geometric origin [4]. Moreover, it predicts an enantio-sensitive ‘molecular compass’ which causes the photoelectron spin to orient differently for opposite enantiomers [5], thereby enabling a ‘locking’ between the photoelectron spin and the orientation of the molecular cation. Our results provide a unified picture of spin-chirality coupling in photoionization and establishes a direct conceptual link to the CISS effect, identifying the fundamental geometric quantities responsible for enantio-sensitive spin-polarization across molecular systems.

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PROBING CHIRAL RECOGNITION IN THE CARVONE-1-PHENYLETHANOL COMPLEX BY ROTATIONAL SPECTROSCOPY

S. Indira Murugachandran¹, M. Eugenia Sanz¹

¹Department of Chemistry, King's College London, London SE1 1DB, UK

Odor perception is often enantioselective. Enantiomers of some chiral odorants smell differently or have a completely different odour threshold. Carvone and 1-phenylethanol (1PE) are widely used chiral fragrance ingredients whose enantiomers smell differently. Their functional groups make their complex an attractive model to investigate the interactions involved in chiral recognition. By applying chirped pulse Fourier transform microwave spectroscopy and quantum-chemical methods, several isomers of (*R*)-carvone...(*S*)-1PE (*RS*) and (*S*)-carvone...(*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 bind through primary O–H...O and secondary C–H... π hydrogen bonds. Homochiral *SS* complexes show an additional C–H...O interaction. Binding and conformational preferences as well as the balance of intermolecular interactions will be discussed.

N: Invited Speakers

Friday, September 04, 2026, 09:00

Chair : Daniel Obenchain

CONNECTING INTERSTELLAR ICE CHEMISTRY TO ASTRONOMICAL OBSERVATIONS: LABORATORY CONSTRAINTS FOR MOLECULAR ASTROPHYSICS

Bernadette M. Broderick¹

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Infrared spectroscopy with the James Webb Space Telescope (JWST) and millimeter-wave observations with the Atacama Large Millimeter/submillimeter Array (ALMA) have transformed our view of molecular complexity in star-forming regions, protoplanetary disks, and icy environments. JWST now reveals the composition and evolution of interstellar ices, while ALMA traces gas-phase molecules released into warm and chemically active regions. However, a central challenge remains: to connect the chemistry occurring within the ice on dust grains to the molecular inventories observed in the gas phase. This is essential both to understand the chemical evolution as planetary systems emerge, and to enable molecular abundances observed in remote regions to report reliably on conditions there. Addressing this challenge requires laboratory experiments that reproduce astrophysical conditions while providing molecular-level detail unavailable from observations alone.

To meet this need, we have developed CPICE (Chirped-Pulse Ice), a laboratory platform designed to bridge solid-state and gas-phase astrochemistry. CPICE combines in situ FTIR spectroscopy of cryogenic ices with chirped-pulse rotational spectroscopy of molecules immediately upon their release during controlled thermal desorption. This dual perspective allows direct comparison between condensed-phase chemistry and the gas-phase products that are accessible to astronomical observation. The instrument is particularly powerful for identifying structural isomers, conformers, and minor reaction products that are difficult or impossible to identify through traditional methods, but may be essential for accurate interpretation of observations. In this presentation, the application of CPICE to investigate several problems of broad relevance to observational astronomy will be described. This includes the energetic processing of nitrile-containing ices under vacuum ultraviolet (VUV) irradiation and keV electron bombardment, simulating the effects of photons and charged particles in interstellar environments. These studies reveal how molecular complexity evolves under different radiation fields and how abundance ratios of related species may preserve information about environmental history. Experiments probing the sublimation of molecules desorbed from icy grains into the gas phase during controlled warm-up will also be described. Temperature-programmed desorption experiments show that sublimation can be non-equilibrium, composition dependent, and in some cases conformer-selective. Such effects, revealed for the first time by CPICE, may influence the inferred gas-phase abundances, excitation conditions, and spectral signatures ultimately observed toward protostars and disks. As the inventory of complex molecules detected in the ISM grows, and new instruments are developed with greater sensitivity and spatial resolution, new tools such as CPICE will be essential to make the most of these observations.

ACROSS WAVELENGTHS AND TOWARDS HIGH RESOLUTION: EXOMOL FOR JWST, ARIEL AND THE ELT ERA

Sergey Yurchenko¹

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

The next phase of exoplanet spectroscopy will combine observations that place very different demands on molecular data. JWST is already revealing chemically and thermally diverse atmospheres through broad-wavelength spectra; Ariel will extend comparative atmospheric studies to large populations of planets; and the Extremely Large Telescope era will exploit Doppler-resolved molecular signatures at spectral resolutions where the positions, intensities and shapes of individual lines become decisive. The challenge is therefore no longer simply to calculate more transitions, but to construct molecular datasets that remain complete, accurate and internally consistent across wavelength, temperature and spectral resolution.

ExoMol is evolving in response to this challenge. I will review its development from a project focused primarily on high-temperature infrared line lists into a broader molecular-data infrastructure, and outline its scientific vision and programme for the years ahead. This programme will extend spectroscopic coverage from the infrared to the ultraviolet; improve high-resolution line positions using empirical energies and uncertainty-aware datasets; incorporate electronic spectra, photodissociation and quasi-continuum absorption; develop data for non-LTE populations and radiative processes; and provide efficient opacity products for atmospheric modelling and retrievals.

Particular attention will be given to the complementary requirements of completeness and precision. Low- and medium-resolution atmospheric retrievals require comprehensive opacity over broad spectral ranges, whereas high-resolution cross-correlation and Doppler spectroscopy require exceptionally reliable frequencies and relative intensities for selected spectral features. Meeting both requirements will demand closer integration of variational calculations, laboratory measurements, spectroscopic networks, atmospheric models and astronomical validation. The goal is to make ExoMol not only a repository of molecular line lists, but a traceable and adaptable molecular-data framework supporting the full chain from fundamental spectroscopy to atmospheric discovery.

O-I: Contributed Talks

Friday, September 04, 2026, 11:00

Chair : Amanda Ross

AI

STARK-SHIFT DOUBLE-RESONANCE SPECTROSCOPY OF EXCITED STATES IN HIGH POLYADS OF METHANE

Vinicius Silva de Oliveira¹, Adrian Hjältén¹, Michael Rey², Yuan Cao¹, Andrea Rosina¹, Kevin K. Lehmann³, Aleksandra Foltynowicz¹

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²ICB, UMR CNRS 6303, Université Bourgogne Europe, Dijon Cedex, France

³Departments of Chemistry & Physics, University of Virginia, Charlottesville, USA

The vibrational energy levels of methane are organized into closely spaced, strongly interacting states known as polyads (P_n , with n numbered with increasing energy). Accurate measurements of Stark shifts allow precise determination of dipole moments of individual states, which can help characterize state mixing and test theoretical models. We report the first measurement of Stark shifts of highly-excited levels of methane in the triacontad (P_6) polyad around 9000 cm^{-1} using frequency-comb-referenced continuous-wave optical-optical double-resonance (OODR) spectroscopy [1] with a $3.3\text{ }\mu\text{m}$ pump laser and a cavity-enhanced $1.67\text{ }\mu\text{m}$ probe laser. Stark plates generate electric field of up to 10 kV/cm over 55.5 cm

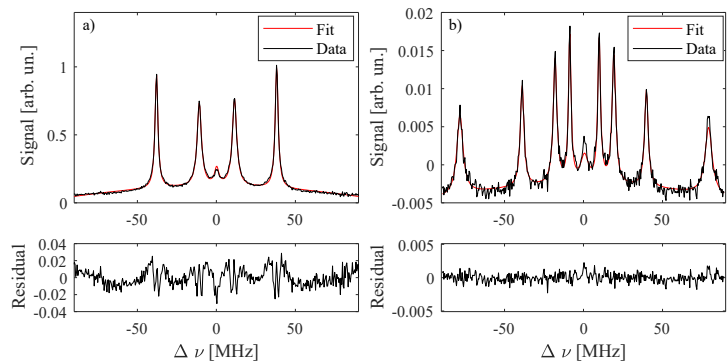


Figure 55: a) A V-type $2\nu_3$ $P(2, E)$ transition at $5983.183412(9)\text{ cm}^{-1}$ reaching P_4 , and b) a ladder-type $3\nu_2 + \nu_3 + \nu_4 \leftarrow \nu_3$ $R(2, E)$ transition at $5909.44048(1)\text{ cm}^{-1}$ reaching P_6 . The pump is tuned to the center of the ν_3 $Q(2, E)$ transition, with pump and probe polarizations aligned parallel to the electric field of 5 kV/cm .

of the 60 cm cavity length. The pump frequency is tuned to the center of an E -symmetry transition in the ν_3 band of methane, while the probe detects sub-Doppler V-type OODR transitions to the tetradecad (P_4) polyad around 6000 cm^{-1} (Fig. 1a), and ladder-type transitions to P_6 (Fig. 1b), whose rest frequencies have been determined previously [2]. We model the individual peaks, corresponding to different projections of the angular momentum $M = -J, -J+1, \dots, J$ on the electric field axis, using Lorentzian line shapes. Peaks corresponding to the co- and counter propagating pump and probe beams have different widths, but fixed ratio of around 5:3 [3]. Using previously determined Stark shift coefficients of the ground and intermediate ν_3 fundamental levels [4,5], we retrieve the Stark shift coefficients of the upper states of the transitions (8 in P_4 and 23 in P_6) from the positions of the peaks. We compare these coefficients to predictions from our zero-field effective Hamiltonian for CH_4 [1,2], combined with a newly-developed *ab initio* effective Stark Hamiltonian $H_{\text{Stark}} = \mu_Z E_Z$, where the space-fixed dipole moment μ_Z is related to the molecular-fixed (MF) *ab initio* effective dipole moment $\mu^{(F_2)}$, composed of vibrational, rotational and Coriolis-type terms, accounting for all polyad transitions up to P_6 . Most of the calculated linear Stark splittings are found to be in excellent agreement with the experimental values.

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FREQUENCY COMB-CALIBRATED ROTATIONALLY RESOLVED SPECTRUM OF THE H₂O–CO₂ VAN DER WAALS COMPLEX IN THE 30H RANGE

A.S. Bogomolov¹, S. Collignon¹, N. Moazzen-Ahmadi², M. Herman³, and C. Lauzin¹

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Water and CO₂ are the most important greenhouse gases in our atmosphere. The solvation of CO₂ 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 a rotationally resolved spectrum of the triple excitation of the OH stretch in the H₂O–CO₂ molecular complex. This represents a further step in our longstanding effort to better characterize the dynamics of H₂O–CO₂ interactions, notably through a systematic increase in vibrational excitation^{1,2,3,4}. Increasing excitation will ultimately drive the isomerization of the complex into carbonic acid H₂CO₃. The complexes were formed from an 8 cm-long pulsed slit supersonic jet and probed by the CRDS technique in the spectral range of the second OH overtone of H₂O, using the FANTASIO setup^{5,6}. A home-built external cavity diode laser (ECDL, near 950 nm, 10600 cm⁻¹), stabilized to the frequency comb, was used as the light source. The recorded spectrum was vibrationally assigned to the $(v_1, v_2, v_3) \leftarrow (v'_1, v'_2, v'_3) = (2, 0, 1) \leftarrow (0, 0, 0)$ and $(2, 0, 1) + \text{intermolecular mode} \rightarrow (0, 0, 0)$ where the v_1, v_2, v_3 are vibrational quantum numbers of the isolated H₂O molecule are used to assign the involved states. In this talk, I will present the experimental spectrum and the improvements to the experimental setup that enabled the recording of this spectral signature. I am going to present our progress in the analysis of this spectrum using group theory and an effective Hamiltonian. Finally, perspectives on crossing the isomerization barrier will be presented.

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OPTICAL GAS THERMOMETRY AND AMOUNT-OF-SUBSTANCE METROLOGY USING CAVITY MODE-DISPERSION SPECTROSCOPY

D. Lisak¹, S. Wójtewicz¹, A. Cygan¹, P. Wcisło¹, R. Ciuryło¹, K. Bielska¹

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High-resolution molecular spectroscopy has recently become a powerful tool for primary gas thermometry and amount-of-substance metrology following the redefinition of the SI system, in which the Boltzmann constant (k) was assigned an exact numerical value. Optical spectroscopic techniques establish a direct link between thermal energy (kT) and measurable molecular spectra, offering traceable, non-contact measurements with high accuracy. Among these techniques, line-ratio thermometry (LRT) has emerged as a particularly attractive approach because it combines high temperature sensitivity with applicability over a broad pressure range.

Recent research [1] demonstrated high-performance LRT with the CO (3–0) vibrational band using cavity mode-dispersion spectroscopy (CMDS) [2,3] and reference *ab initio* line intensities [4]. The resonance frequencies of a high-finesse optical cavity provide frequency calibration for both spectral axes, ensuring direct traceability to primary frequency standards while enabling highly reproducible line-shape and line-intensity measurements. We show that using new state-of-the-art *ab initio* transition intensities [5], this approach enables temperature measurements with an uncertainty below 20-mK at room temperature.

The combination of accurate thermometry with absolute molecular line intensities also enables fully optical determination of gas concentration with permille-level precision over pressures ranging from 50 Pa to 20 kPa. Compared with Doppler broadening thermometry (DBT), this substantially extends the operating pressure range while preserving the advantages of an optical, non-invasive, and species-selective measurement technique. Such capabilities make CMDS-based LRT an attractive candidate for future primary realizations of both the kelvin and the mole.

Finally, we discuss the present limitations arising from spectroscopic models [6] and reference molecular parameters [5,7], together with current efforts aimed at improving theoretical predictions and experimental spectroscopy. These developments are expected to further enhance the accuracy, robustness, and practical applicability of optical primary thermometry and amount-of-substance metrology.

The research was supported by the state budget of Poland, allocated by the Minister of Education and Science under the "Polska Metrologia II" program, project no. PM-II/SP/0011/2024/02, and the European Partnership on Metrology project "22IEM03 PriSpecTemp".

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CAVITY-ENHANCED SPECTROSCOPY IN THE DEEP CRYOGENIC REGIME FOR QUANTUM SENSING AND METROLOGY

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High-finesse cavity-enhanced spectrometers play a crucial role in both fundamental research and practical applications. Lowering the system's operating temperature from room temperature to the deep-cryogenic regime provides substantial advantages for spectral measurements, such as narrowing the Boltzmann distribution of rotational states, suppressing Doppler broadening, enhancing peak absorption and freezing out unwanted molecular species. We present the first cavity-

enhanced spectrometer designed to operate entirely within the deep-cryogenic regime, reaching temperatures as low as 4 K [1] (Fig.1). In our system, the entire optical cavity, including the mirrors and piezo actuator stack, is cooled uniformly along with the gas sample, ensuring that the sample stays in thermodynamic equilibrium [2]. With it we performed a Doppler-limited spectroscopy of the S(0) (1-0) rovibrational transition in molecular hydrogen, reaching unmatched agreement with the latest theoretical prediction within its stated uncertainty. This level of consistency probes molecular quantum theory at the tenth significant digit and, to the best of our knowledge, provides the most precise validation of quantum electrodynamics in a four-body system to date [3].

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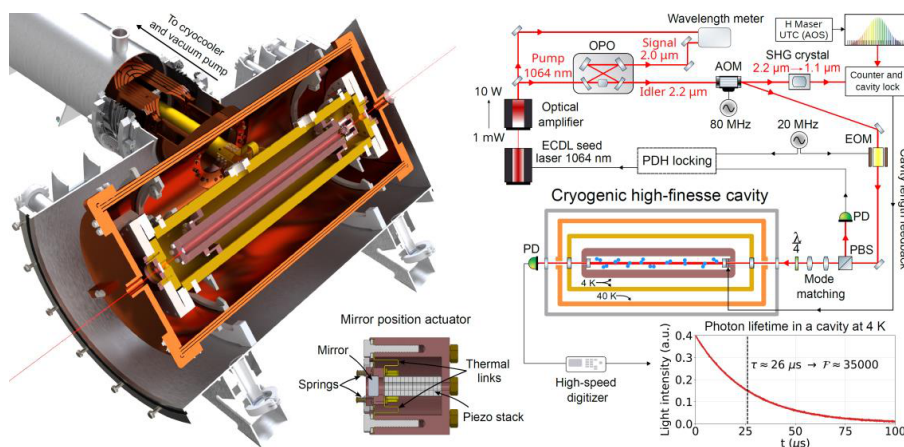


Figure 56: Spectrometer based on a cryogenic high-finesse cavity. (left panel) Illustration of the cryogenic part. (right panel) Simplified scheme of the experimental setup.

SUB-KHZ VIBRATIONAL FREQUENCY MEASUREMENTS VIA MID-INFRARED SATURATION ABSORPTION SPECTROSCOPY

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At LPL, a sub-Hz-level 10 μm quantum cascade laser (QCL) has been stabilized to an SI-traceable 1.54 μm metrology-grade frequency reference signal. This reference is provided by the French metrology institute and delivered via a noise-compensated 26-km-long fiber optic link of the REFIMEVE national research infrastructure¹. Using an optical frequency comb, the spectral purity and stability of the near-infrared (NIR) reference source are transferred to the mid-infrared (MIR) region, achieving a relative frequency uncertainty of 10^{-14} and QCL linewidth to 0.1 Hz^{2,3}. This ultra-stable MIR-QCL has been employed for high-resolution spectroscopy on various molecular species using sub-Doppler saturated absorption spectroscopy³. This system, operable within both an optical cavity and a multipass absorption cell, achieves line center frequency uncertainties ranging from a few kilohertz to a few ten hertz.

In this report, we present recent high-resolution spectroscopic studies of methanol, ammonia, and ethylene. These measurements significantly enhance and refine molecular databases and are as well steps toward testing fundamental physics. Current efforts include investigating potential variations in the electron-to-proton mass ratio⁴ and testing parity symmetry by measuring the tiny parity-violating energy differences between enantiomers of chiral molecules⁵. Additionally, we discuss ongoing developments involving a new generation of MIR modulators⁶ to further advance spectroscopic measurement capabilities.

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METROLOGY OF THE HELIUM DIMER WITH A SPECTRAL RESOLUTION OF 2.5 PPB AND A PRECISION OF 15 PPT

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The helium dimer (He_2) serves as a benchmark system for testing ab initio calculations. Recently, highly accurate first-principles calculations that include relativistic and quantum-electrodynamical (QED) effects have become feasible for this six-particle, four-electron molecule [1-3]. Accurate experimental data on the low-lying triplet electronic states of He_2 are needed to validate the current theoretical advances.

We report on a high-resolution spectroscopic study of the $b\ ^3\Pi_g(v=3) - a\ ^3\Sigma^+(v=0)$ transition of He_2 in the near infrared (NIR) around 1040 nm. The measurements built upon the recently developed Doppler-free method of imaging-assisted single-photon spectroscopy (IASS) [4] and applied it for the first time to a molecule. This generalized method can be applied to arbitrary single-photon transitions of atoms and molecules in the gas phase. A narrowband continuous-wave laser locked to a frequency comb referenced

to an SI-traceable frequency standard [5] was used in combination with an automatic interferometric alignment of the two counterpropagating laser beams using a Michelson-type interferometer featuring a corner cube, as described in Ref. [6]. With this setup, each spectral line was split into a red-shifted (ν_r) and a blue-shifted (ν_b) component with the first-order-Doppler-free line center $\nu = (\nu_r + \nu_b)/2$. To optimize the spectral resolution, each Doppler component was further split into sub-Doppler components by imaging the photoexcited molecules in the direction perpendicular to both the laser and the molecular beams. Integration of the recorded signal along the forward propagation axis of the molecular beam led to images as shown below. The Doppler-free transition frequency was extracted using a Radon transform and a cross-correlation analysis, leading to full widths at half maximum of only 700 kHz and the determination of line centers with a precision of a few kHz.

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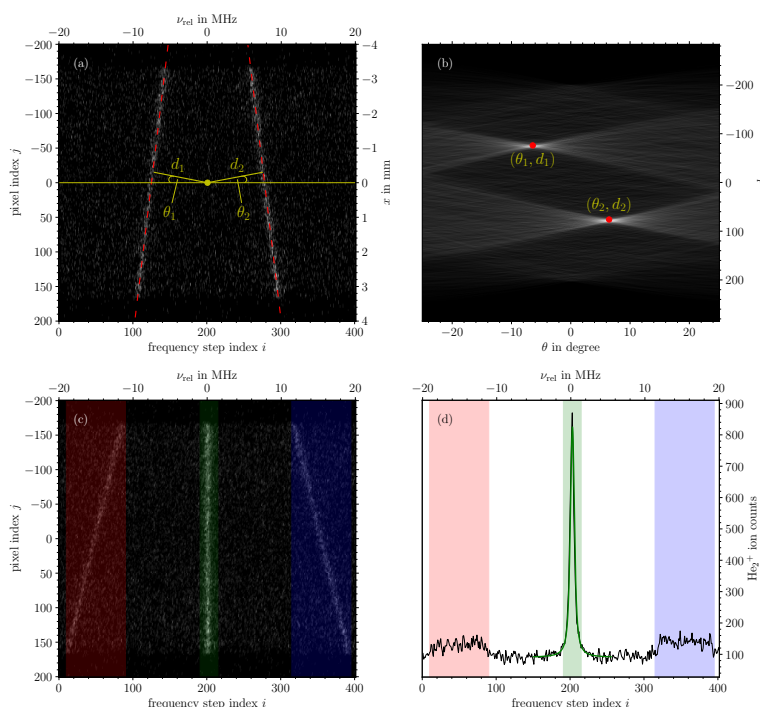


Figure 57: Illustration of the Radon transform with the example of the $b(v=3, N=1, J=2) \leftarrow a(v=0, N=1, J=2)$ transition of $^4\text{He}_2$.

O-II: Contributed Talks

Friday, September 04, 2026, 11:00

Chair : Mattia Melosso

AII

FIRST LIGHT OF A NEW 5.5–18 GHz BROADBAND CRYOGENIC BUFFER GAS COOLING CP- FTMW SPECTROMETER

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Chirped-pulse Fourier Transform Microwave (CP-FTMW) spectroscopy, with supersonic jet-cooling, has been the workhorse for pure rotational spectroscopy over the last two decades. It is a versatile technique that introduced orders of magnitude of gain in speed, and true broadband capabilities compared to the long-used cavity techniques.

Cryogenic Buffer Gas Cooling (BGC) is an approach that can bypass some of the constraints of a pulsed-jet setup and achieve high sensitivity and fast acquisition speeds. It provides a continuous, high-density ensemble of molecules collisionally thermalized with buffer gas at ~ 7 kelvin, enabling real-time data acquisition with exceptional sensitivity. Here, we present the design, construction, and initial operation of a novel cryogenic BGC-CP-FTMW spectrometer spanning a broadband coverage of 5.5-18 GHz. To demonstrate its sensitivity, we report the successful detection of several low-dipole moment molecules, increasing the accessibility of these types of molecules.

SIX-FOLD METHYL INTERNAL ROTATION AND ^{14}N NUCLEAR QUADRUPOLE COUPLING IN THE MICROWAVE SPECTRA OF N-METHYLMALEIMIDE AND N-METHYLSUCCINIMIDE

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Succinimides and maleimides are highly functionalized cyclic organics that are important in biological chemistry and organic synthesis. Understanding their isolated gas-phase structures is crucial to revealing fundamental properties that may correlate with processes involved in their chemical and biological activities. In this work, we present the high-resolution rotational study of *N*-methylmaleimide (MMI) and *N*-methylsuccinimide (MSI) using a combination of spectroscopic techniques: a molecular jet K_a -band Chirped Pulse Fourier-Transform Microwave (CP-FTMW) [1] spectrometer and two resonator-based FTMW instruments (Passage And Resonance In Synergy–PARIS [2] and K_a -band “small cavity” [3]). In both molecules, the methyl group undergoes facile internal rotation, splitting each rotational transition into the $m = 0$ and $m = 1$ torsional species. For MMI, a total of 672 lines were assigned from the PARIS and “small cavity” measurements, and fitted to an rms deviation of 89.1 kHz using the *XIAM* program. [4] Local separate fits of the two torsional species confirmed the correctness of the assignment. The program *BELGI- C_s -hyperfine* [5] reduced the rms deviation to 4.5 kHz, consistent with the measurement accuracy. For MSI, 260 transitions were assigned from the K_a -band CP-FTMW spectra with a measurement accuracy of 25 kHz. The data were fitted first with the *XIAM* program to an rms deviation of 32.7 kHz, and then with the *BELGI* program, which reduced this value to 24.9 kHz. The V_6 torsional barriers were determined to be 20.2364(16) cm^{-1} for MMI and 25.833(11) cm^{-1} for MSI. These values are significantly lower than that of *N*-methylpyrrole (67.8 cm^{-1}), suggesting that the two adjacent carbonyl substituents enhance the sensitivity of the methyl rotor to the local C_{2v} electronic environment, thereby lowering the torsional barrier.

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THIONATION TO THIOPIVALIC ACID: FROM SYNTHESIS TO A BROAD MICROWAVE ANALYSIS USING A VARIETY OF SPECTROSCOPIC TECHNIQUES

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Recent studies of thiobenzoic¹ and thioacetic² acid with sulphur trioxide have led to the discovery of an in-situ reaction inside the collision region of a jet expansion. An unexpected landscape of isomers including O-S and S-S bonded sulfuric acid anhydrides was found in the case of thioacetic acid and believed to form within a complex reaction mechanism which likely depends on participation by higher clusters and further work on thionated derivatives is, therefore, of interest. Thiopivalic acid, (CH₃)₃CCOSH, was therefore prepared using phosphorous pentasulfide (P₂S₅) and analysed using a variety of spectroscopic techniques. Negative soft ionization mass spectroscopy suggests a high yield of thiopivalic acid (95%) with possible anhydrous dimers alongside phosphorous-sulfide-oxide byproducts. Subsequent bulk phase IR and NMR analysis confirm the near complete conversion in the thionation and ruling out any significant amounts of dimers.

We report the supersonic jet microwave spectrum of thiopivalic acid in the region of 6-18 GHz using chirped pulse and narrow-band cavity measurement techniques. The dense spectra of the reaction product features lines corresponding to calculated rotational constants for thiopivalic acid, establishing an unambiguous assignment among non assigned lines likely related to byproducts. The conformational landscape, calculated with *Gaussian16*³ at the M06-2X/cc-pVTZ level, yielded four possible structures between a *syn*- and *anti*-configuration of the thiol or thione group. Whereas only the thiol isomers plausibly populated at 2 K experimental temperature, merely the thiol-*syn* conformer was observed in the spectrum, estimated to be lower by 1.67 kcal mol⁻¹ than the *anti*-conformer. Interestingly, despite featuring methyl groups at particularly high barriers, each line occurred as a doublet related to a large amplitude motion of the lowest vibrational normal mode that describes a torsional wagging between the thiol group and the tert-butyl group. Unfortunately, the *c*-dipole moment component affected by this puckering is too small for the cross-tunnelling *c*-type transitions to be measurable, allowing for the assignment of *a*-type and *b*-type transitions featuring Coriolis splittings only. Nevertheless, ΔE was approximated to 20 MHz through a series of fits with a fixed value and floating all other parameters, using the *SPFIT* suite of programs⁴, resulting in two separate fits with two distinct sets of molecular parameters with a fit quality near experimental resolution.

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MICROSOLVATION AND STRUCTURAL EVOLUTION OF METHYL ETHYL AND DIETHYL SULFOXIDES IN WATER CLUSTERS PROBED BY ROTATIONAL SPECTROSCOPY

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Water clusters serve as fundamental model systems for exploring the microscopic structure and formation rules of hydrogen-bonded networks, offering unique insight into microsolvation. Sulfoxide-containing molecules are excellent solute models for such investigations, as their highly polar S=O group provides a strong, directional binding site that anchors and organizes these hydrogen-bonded networks¹. Furthermore, the possibility of tuning their symmetry and chirality by modifying the alkyl substituents allows a direct evaluation of how intrinsic solute properties influence the resulting microsolvation structures and interaction patterns.

Herein, we employed a combination of rotational spectroscopy and quantum-chemical methods to investigate the conformational landscape of the methyl ethyl sulfoxide (MESO) and diethyl sulfoxide (DESO) monomers, as well as their microsolvated clusters with up to five water molecules. The conformer-rotamer ensemble sampling technique (CREST)² together with geometry optimizations at the B3LYP-D4/def2-QZVP level of theory using the ORCA 5.0.4 program package³ was employed to predict energetically low-lying conformers. The rotational spectra of MESO/DESO monomers and their sulfoxide-(H₂O)_n clusters (*n* = 1–5) were recorded using the chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer, assigned and the cluster topologies were structurally determined. For the *n* = 1–3 clusters, the water molecules are primarily anchored to the sulfoxide oxygen atom through strong S=O ··· H-O hydrogen bonds, giving rise to chain-like hydrogen-bonded structures further stabilized by weak C-H ··· O interactions. For the larger clusters (*n* = 4–5), the observed structures are consistent with cyclic water networks, where the water molecules form cyclic hydrogen-bonded rings interacting with the sulfoxide group and alkyl moieties through hydrogen bonds and weak noncovalent interactions. MESO/DESO do not significantly disturb the ring-like structures of water tetramers and pentamers, retaining the cyclic motifs observed in pure water clusters. The MESO/DESO–water clusters may serve as simple model systems for understanding the solute–water interactions of sulfoxides in aqueous environments relevant to atmospheric processes.

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ROTATIONAL OBSERVATION OF OPEN-SHELL SINGLET PERSISTENT RADICAL PAIRS

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Radicals, characterized by unpaired electrons, are highly reactive species that serve essential functions across combustion, polymerization, and atmospheric chemistry. Their chemistry frequently proceeds through radical pairs—transient intermediates positioned in close proximity that exhibit intriguing electronic properties.^{1,2} In particular, whether these pairs adopt singlet or triplet spin states profoundly influences their propensity to recombine or engage in alternative reaction pathways.³ However, the ultra-short lifetimes of radical pairs have historically rendered them inaccessible to direct experimental observation. Here we report the first gas-phase detection and structural characterization of radical pairs (Figure 1), isolated within the collision-free, cryogenic environment of a supersonic molecular jet. The persistent nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was chosen as the model system. Using isotope-sensitive high-resolution rotational spectroscopy, we identified two distinct pairing configurations.⁴ In each dimer, the nitroxyl units engage in non-covalent interactions with N···O separations of 3.38 and 4.93 Å, respectively; these assignments were corroborated by multiple ¹⁸O-labelling experiments. Remarkably, the absence of electron spin hyperfine effects aligns with quantum mechanical density functional theory predictions that favor an unexpected open-shell singlet configuration. These findings offer the first direct molecular-level picture of isolated radical pairs and pave the way for new explorations into the quantum structure and reactivity of correlated radical species.

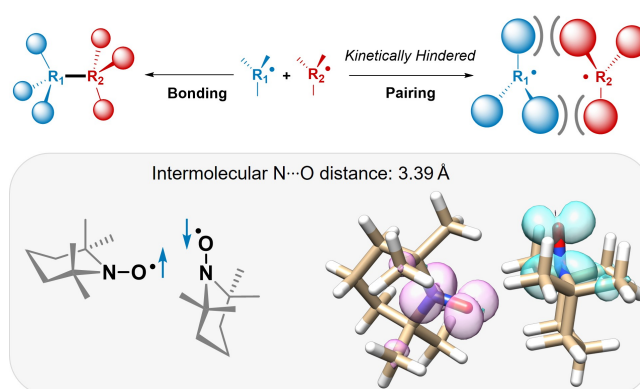


Figure 58: Kinetically hindered radical pairs formed from persistent radical TEMPO

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NON-COVALENT INTERACTIONS OF PHTHALIDE HYDRATES STUDIED BY ROTATIONAL SPECTROSCOPY

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Phthalide plays an important role in the pharmaceutical and agricultural industries as a synthetic precursor for compounds such as antidepressants, pesticides, and fungicides. Chemically, it is considered the simplest benzolactone, composed of a benzene ring and a lactone functional group. We have investigated the phthalide monomer and its complexes with up to four water molecules using Fabry-Perot and chirped-pulse Fourier transform rotational spectroscopy supported by quantum-chemical calculations. As the number of water molecules increases, their preferred location changes to establish interactions both with the carbonyl oxygen and the electron density of the furanone ring. Our results on phthalide-(H₂O)_{1–4} structures and non-covalent interactions inform on the first stages of solvation and help understanding the influence of competing binding sites on this process.

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